

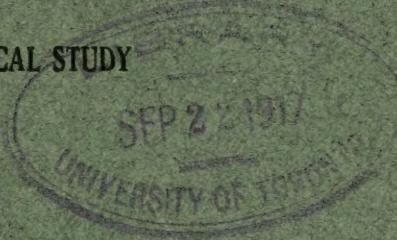
*U.S. MINES BUREAU*

Bulletin 133

DEPARTMENT OF THE INTERIOR  
FRANKLIN K. LANE, SECRETARY  
BUREAU OF MINES  
VAN. H. MANNING, DIRECTOR

THE WET THIOLINE PROCESS FOR RECOVERING  
SULPHUR FROM SULPHUR DIOXIDE  
IN SMELTER GASES

A CRITICAL STUDY



BY

A. E. WELLS

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of the first kind of persons except for the slaves of slaves and of the second  
kind of persons, who are the slaves of slaves, and others, called by those  
of the first kind, masters, which were originally mentioned in the  
second kind of persons, and number not less than seven.  
The masters of their slaves, who are the slaves of slaves, and of the second  
kind of persons, and of the slaves of slaves, are called by those who are  
the slaves of slaves, masters, and others, called by those who are  
the slaves of slaves, slaves.

# THE WET THIOGEN PROCESS FOR RECOVERING SULPHUR FROM SULPHUR DIOXIDE IN SMELTER GASES; A CRITICAL STUDY.

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By A. E. WELLS.

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## INTRODUCTION.

A critical study of the wet Thiogen process for extracting sulphur from the smoke of smelters is one of several investigations related to the general smelter-smoke problem that are being conducted under the direction of the Bureau of Mines. Part of the work done in the pyrometallurgical section of the cooperative metallurgical exhibit of the Bureau of Mines at the Panama-Pacific International Exposition during 1915 related to this investigation, and at the expiration of the exposition, the work was continued in the laboratories of the Bureau of Mines in the Hearst Memorial Mining Building of the University of California, Berkeley, Cal., where a mining experiment station of the bureau has been established under the cooperative agreement with the University of California.

Early in the spring of 1915, when plans were being made to cooperate with several metallurgical interests, the Thiogen Co. proposed to the Bureau of Mines that, along with the studies of various proposed methods for eliminating sulphur dioxide from smelter smoke, there should be included a study of the wet Thiogen process. In the study as outlined it was proposed to determine whether it would be technically and commercially feasible to use the process for the recovery of elemental sulphur from the sulphur dioxide in waste smelter gases.

Although there had been no large-scale work with the process, either in the laboratory or at a smelter, representatives of the metallurgical and mining industry had shown considerable interest in the proposed method, and the desire had been expressed that a better knowledge of the possibilities of the process should be obtained. Thus, cooperation with the Thiogen Co. seemed justified by the interests of the metallurgical industry, and by the conservation promised by the recovery of a product of market value from what is otherwise a waste, and in some instances a serious nuisance.

In accepting the responsibility for directing this investigation, the officials of the Bureau of Mines were necessarily free to conduct the work in the manner they considered necessary to determine the facts. It was also understood that any information obtained was to be made available to all who might be interested and might be printed in a Bureau of Mines report. To cover the cost of laboratory equipment and supplies, and the payment of salaries of assistants, other than Bureau of Mines employees, the Thiogen Co. in May, 1915, deposited with the cooperative metallurgical exhibit fund a sum considered sufficient to warrant starting the laboratory investigation. The origin and organization of this fund has been described by Clevenger and the author.<sup>a</sup>

In outlining the program for this investigation it was hoped that ultimately a small complete plant would be erected and the investigation center around the operation of the plant. However, preliminary to the erection of the plant, a laboratory study of the process was considered necessary, as the technical features of the process could be determined, it was believed, as satisfactorily on a smaller scale as on the scale first proposed. However, it was realized at the time that it would not be possible to determine so satisfactorily or definitely the commercial possibilities of the process on the scale of work adopted as in the larger operating plant. With this fact in mind it was planned that, if the study of the technical features on a laboratory scale gave sufficient promise of the process being commercially feasible, an operating unit should, if possible, be constructed later, and that more definite information concerning the commercial prospects should be determined.

The investigations were started in June, 1915. In June and July work was confined entirely to small-scale laboratory tests, in which a careful study of the chemical reactions involved was made. In August, tests on a larger scale were started, and these were continued until December, small-scale tests being made at the same time.

On December 1, 1915, all work on the Thiogen process was discontinued temporarily, as the close of the exposition necessitated moving the laboratories. Work on the Thiogen process was started again in January, 1916, in the laboratories of the new mining experiment station at Berkeley, Cal., and was continued during the spring of 1916 until a point was reached where it was felt that the essential parts of the process had been carefully covered, and that some definite statements concerning the technical features and possibilities of the process, as given in this report, were warranted.

<sup>a</sup> Clevenger, G. H., and Wells, A. E., The cooperative metallurgical exhibit at the Panama-Pacific International Exposition: Met. and Chem. Eng., vol. 13, Oct. 15, 1915, p. 743.

### THE TWO THIOGEN PROCESSES.

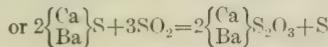
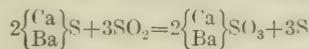
The Thiogen Co. has two processes,<sup>a</sup> both based on the same general chemical reactions, but differing widely in their application and possibilities.

In the dry Thiogen process, sulphur dioxide of suitable concentration is mixed with hydrocarbon gas, or practically any refining gas, and the mixture is passed over a heated sulphide such as calcium sulphide, or barium sulphide. In the reaction that takes place, resulting in the reduction of the sulphur dioxide to sulphur, the sulphide plays simply a catalytic or cyclic role.

On account of its various and limiting factors the dry process seems applicable only to gases of high and uniform sulphur dioxide concentration, and offers fewer chances for practical application than does the wet process.

### GENERAL PRINCIPLES OF WET THIOGEN PROCESS.

The wet Thiogen process is based on the fact that when an alkaline-earth sulphide, as calcium or barium sulphide, either in finely divided water suspension or in solution is added to a solution of sulphur dioxide, the following reaction takes place.



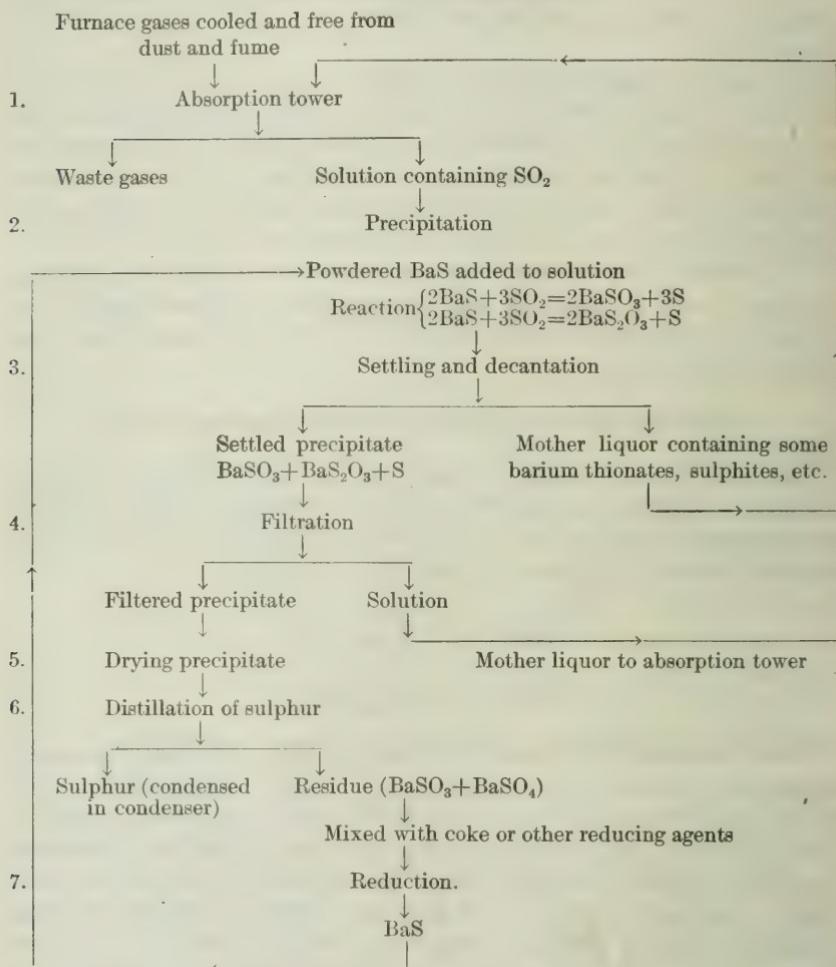
Thus, the sulphur dioxide must first be removed from the gases by absorption in water or mother liquor. This is accomplished in an absorption tower, after the gases have been cooled and cleared of dust and fume. To the solution of sulphur dioxide is added powdered barium or calcium sulphide, when the reactions given above takes place. The precipitate containing the sulphite, thiosulphite, and sulphur is settled, and the mother liquor returned to the absorption tower. The settled precipitate is then filtered and dried. The elemental sulphur and one-half the sulphur from the thiosulphate is distilled, and the sulphur vapors are condensed. The residue, consisting of barium or calcium sulphite and sulphate, is then reduced to the sulphide, which is returned to the operation as a precipitant.

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<sup>a</sup> See Fulton, C. H., Metallurgical smoke: Bull. 84, Bureau of Mines, 1915, pp. 72-77.

The sequence of the operations involved is given in the following diagram:

*Flow sheet of wet Thiogen process.*



#### OUTLINE OF INVESTIGATION.

This investigation was confined to a study of the seven distinct operations of the complete process as indicated in the flow sheet, these operations being as follows:

1. Absorption of sulphur dioxide from furnace gases in water or in mother-liquor solution.
2. Precipitation by incorporating barium sulphide, either in solid form or in solution, into the solution of sulphur dioxide.
3. Separation of the precipitated sludge from the bulk of the mother liquor by settling, the mother liquor being decanted and returned to the absorption tower.

4. Filtration, or dewatering precipitate.
5. Drying precipitate.
6. Distillation of sulphur from precipitate and recovery of elemental sulphur.
7. Reduction of barium sulphite and sulphate to sulphide, the sulphide being returned to the precipitation operation.

Cooling the furnace gases and freeing them from dust and fume by electrical precipitation, filtration through bags, or otherwise have not been considered parts of this investigation. This process starts with the delivery of the cooled and cleaned gases to the absorption tower.

Before entering on a discussion of the investigation it may be well to state briefly why the use of calcium as a precipitant was early discontinued and why barium was used in nearly all of the work.

From some preliminary small-scale laboratory tests it was determined that the reaction between calcium sulphide and sulphur dioxide did not proceed strictly according to the two reactions mentioned above and that there were formed large quantities of thiosulphate and thionates, as well as sulphite, which were readily soluble. The solution of these calcium salts raised the specific gravity of the mother liquor to the point that the settling of the precipitate was very slow and filtration was unsatisfactory. The action of the calcium salts was similar to that found by the chemists of the Thiogen Co., and thus, as was done by them, work with calcium salts was abandoned, the barium salts being used exclusively in the investigation.

#### **ABSORPTION OF SULPHUR DIOXIDE IN WATER OR MOTHER-LIQUOR SOLUTIONS.**

In the investigation the primary object in erecting an absorption tower was to provide sulphur-dioxide solutions for precipitation and subsequent treatment. At the same time it was desired to determine the maximum concentration of sulphur dioxide that could be obtained in the solution coming from the tower with different concentrations of sulphur dioxide in the gases going to the tower. Whether the sulphur dioxide was completely removed from the gases at the same time that saturated solutions were obtained was of secondary importance. As is shown below, the gases were not cleaned completely of their sulphur-dioxide content in any of the tests, and complete recovery of the sulphur dioxide was approached only when the volume of the resulting solution was so large that the solution was not saturated.

Experience with this tower showed that in order to get nearly saturated solutions and at the same time to absorb more completely the total sulphur dioxide in the gases handled it would be necessary to increase either the height of the absorption column or its cross-sectional area, or possibly to change the character of the tower

filling; or, in other words, to bring about any change that would have increased the length of time that a larger volume of liquid would be in contact with the gases.

The absorption results obtained in this tower can be obtained in a larger tower of the same type, correspondingly larger volumes of gases being handled and the velocity of the gases through the tower and the sizes and shapes of tower filling-material being the same. For this reason the absorption data obtained are worth recording.

#### DESCRIPTION OF ABSORPTION TOWER.

The absorption tower used in all of these tests was built of kiln-dried redwood. The inside dimensions were 20.3 by 20.3 centimeters, or 411 square centimeters (8 by 8 inches, or 64 square inches). The tower was composed of five 10-foot sections. The sides of the tower were screwed together and the joints caulked with white lead. Four of the sections were filled with a grill work of wooden blocks 2.5 centimeters (1 inch) square in cross section and 19 centimeters ( $7\frac{1}{2}$  inches) long, placed in the tower so that their diagonal axes were horizontal and perpendicular. Three and one-half blocks constituted a unit, the blocks being attached to a light wooden frame which just fitted the inside of the tower. In each unit the distance between the edges of two adjacent blocks was 1.90 centimeters ( $\frac{3}{4}$  inch).

The area open for the passage of gases between the edges of the block in any unit was 148 square centimeters (23 square inches). Each unit of block was placed in the tower at right angles with and touching the unit immediately above and below. Each alternate unit was staggered; that is, if in one unit the half block was against one side, in the second unit above or below, the half block was placed against the opposite side. Thus, there were no places through the tower where the solution could drop more than a few inches without impinging on the sloping sides of the blocks. This cascading served to keep the blocks moistened. At the same time the ascending gas currents had no path of lesser resistance, and the velocity up through the tower was nearly the same at all parts. It is evident that though this tower filling may be improved, yet this type of packing gives an effective contact of gas and water for the absorption of the sulphur dioxide.

The total surface area in each unit was 838 square centimeters (130 square inches, or 0.905 square foot). There were 340 of these units in the tower; thus the total surface area exposed equaled 28.5 square meters (307 square feet), being 2.88 times greater than if the tower had contained no filling.

At the exposition laboratory the tower sections were erected in one vertical column 50 feet high, the 10-foot section with no block filling being at the bottom. The joints between the sections were made as nearly water and gas tight as possible by careful calking. The gases were blown into the tower at a point about 6 feet above the base, the space below the gas intake serving as a sump for the sulphur dioxide solution.

The water or solutions used for absorption were lifted in a single stage to the top of the tower by a small gear pump. If larger volumes of water were used than the quantity the pumps could handle, hose attachments were made to the water-service lines of the building.

As there was not sufficient headroom for a 50-foot column in the laboratory at the mining building, University of California, the tower was erected in two parts, each having a 5-foot section without grill work at the base and two 10-foot sections filled with the grill work above. The gases issuing from the top of the first part were conducted through an iron pipe to the bottom of the second part. The solutions were first pumped to the top of the second part and thus came in contact with the weakest gases. The solution from this part was then pumped to the top of the first part, whence it ran out into precipitation vats. (See fig. 1 and Pl. I, A).

#### SOURCE OF SULPHUR DIOXIDE GAS.

In all these tests the gases containing the sulphur dioxide were drawn from a small multiple-hearth roasting furnace,<sup>a</sup> in which pyrite ores, screened through a one-fourth-inch screen, were being roasted. In order to increase the concentration of the sulphur dioxide in the gases, elemental sulphur was added at times to the ore charge to the furnace. The sulphur dioxide content of the gases varied between 1 and 15 per cent, but in most of the tests ranged between 6 and 10 per cent.

During the tests at the exposition laboratory the furnace gases were cooled by being passed through a lead-lined tower containing lead coils, built according to a design of Messrs. A. M. Hunt and D. E. Fogg. The gases were passed through the spaces between the series of horizontal lead coils, inside of which water was being circulated.

In the work at the laboratory in the mining building of the University of California the gases were cooled by being passed through 70 feet of 5-inch black-iron stovepipe. The gases were drawn from the roasting furnace through the cooling system by a fan at the tower, which delivered them directly into the tower.

<sup>a</sup> This furnace was loaned by Mr. Utley Wedge and is described on pp. 41-44.

No attempt was made to scrub the gases completely of their entrained solid matter. However, most of the dust settled, and as the material being roasted was nearly pure pyrite, there was little metallic fume carried over into the absorption tower.

Velocity determinations and temperature readings were made and samples of gases for analyses were taken at the fan, on the suction side.

Except during the tests when water was used as the absorbing liquid, the main object of the work with the absorption tower was to

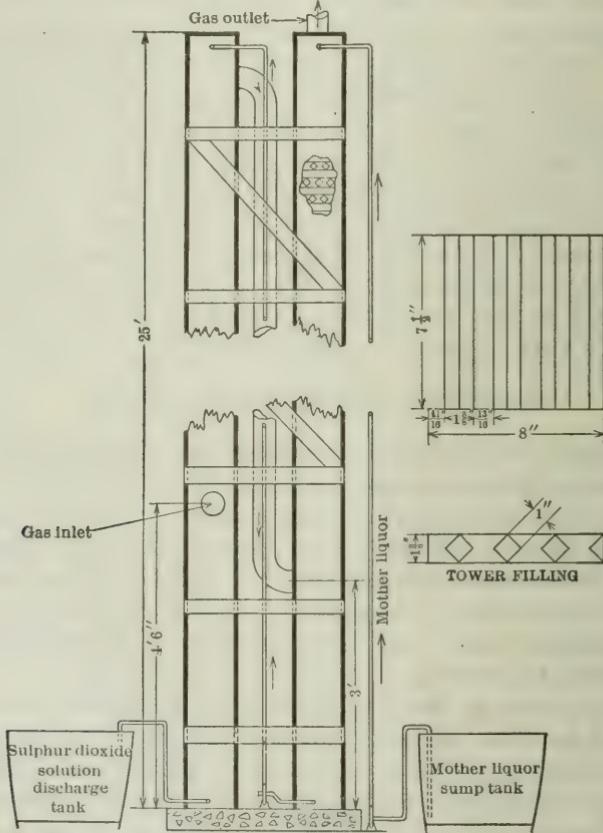
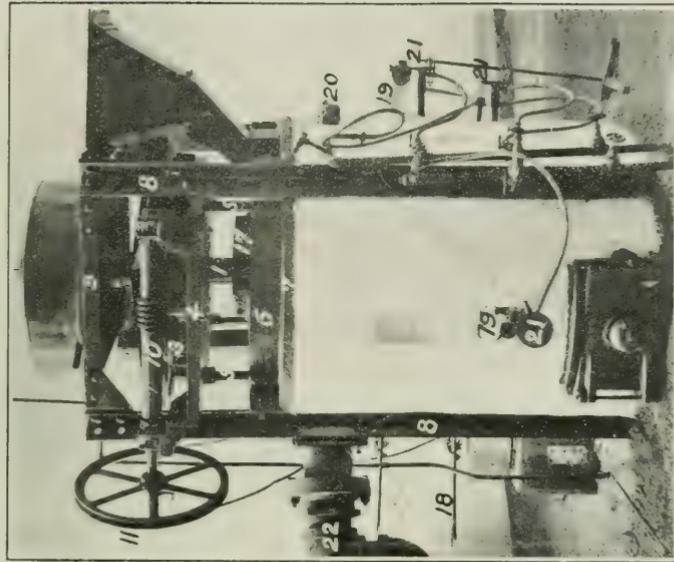


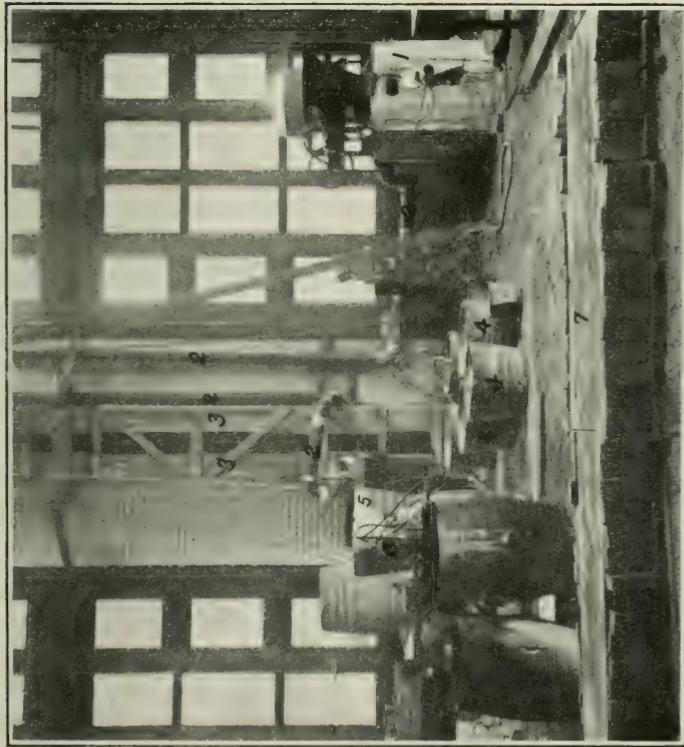
FIGURE 1.—Elevation and details of absorption tower used in experiments.

obtain a sulphurous-acid solution for use in precipitation. However, in all tests in which it was possible, the following records were taken, nearly simultaneously, in order to indicate the efficiency of the tower for absorption purposes:

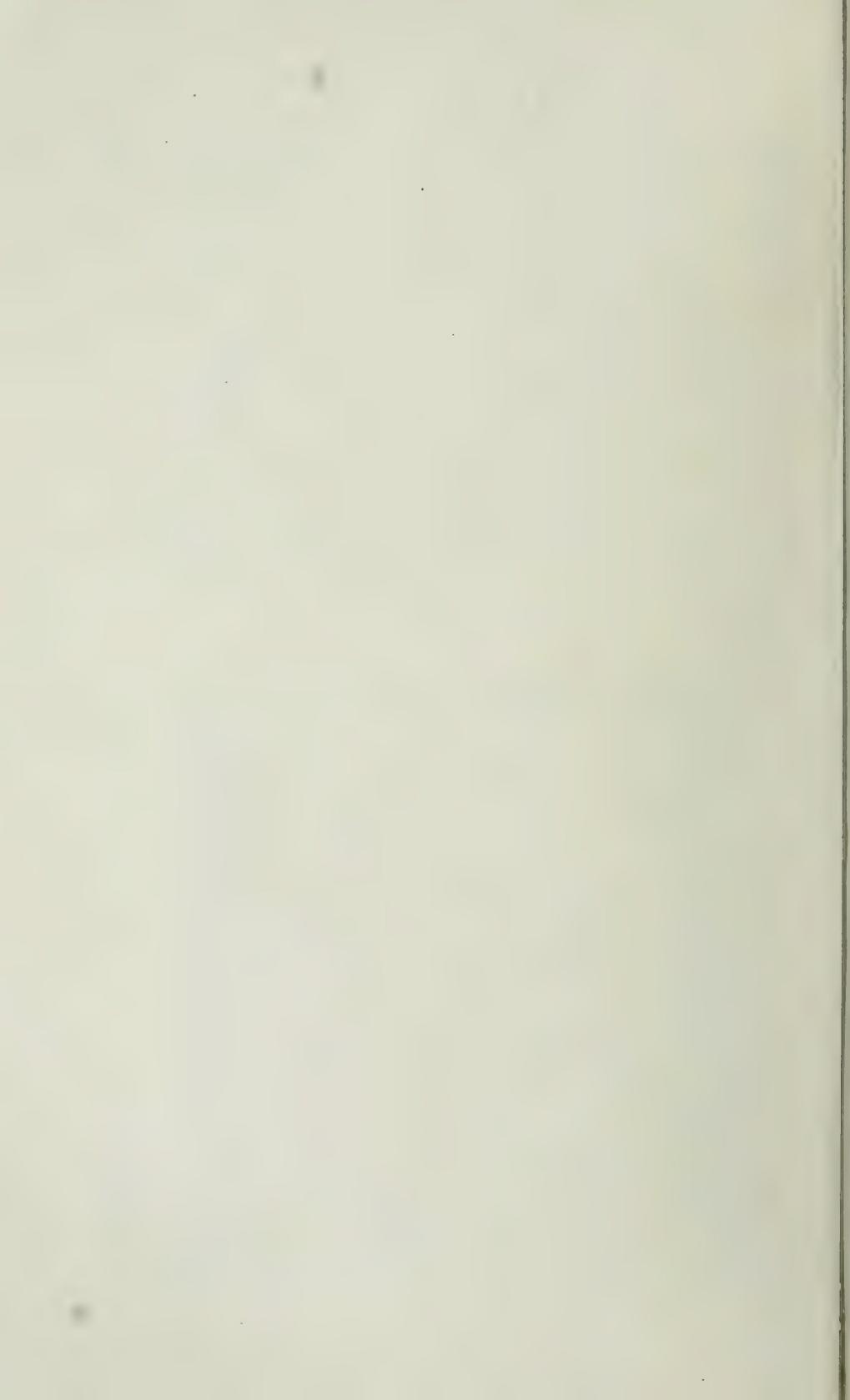
1. Volume and  $\text{SO}_2$  content of gases to tower.\*
  2. Volume, temperature, and  $\text{SO}_2$  content of solution from tower.
- In certain tests, the  $\text{SO}_2$  content of the exit gases from the tower was also determined.



B. MULTIPLE-HEARTH ROASTING FURNACE USED IN TESTS.



A. APPARATUS FOR STUDY OF WET THIOPEN PROCESS: 1, MULTIPLE-HEARTH ROASTING FURNACE; 2, PIPES FOR COOLING GASES; 3, ABSORPTION TOWER; 4, PRECIPITATION TUBS; 5, FILTER TUBS; 6, SUCTION PUMP; 7, DRYING PLATES.



### ABSORPTION OF SULPHUR DIOXIDE IN WATER.

In October, 1915, at the exposition laboratory, tests were made to determine the maximum concentration of sulphur dioxide that could be obtained when water was used as an absorber, corresponding to different concentrations of sulphur dioxide in the gases.

In the tests the total volume of gases going to the tower was varied between 20 cubic feet (566 liters) per minute and 30 cubic feet (850 liters) per minute, the velocity of the gases through the tower thus varying between 1.5 feet (45.8 centimeters) per second and 2.2 feet (67.1 centimeters) per second. The average velocity was 2.0 feet (61 centimeters) per second. The volume of water passing through the tower was varied between 4 liters (1.05 gallons) and 15.5 liters (4.1 gallons) per minute. With a volume of about  $8\frac{1}{2}$  liters per minute being pumped into the top of the tower, the total volume of water in the tower at any one time was about 20 liters (5.3 gallons). The water temperature varied between  $15^{\circ}$  and  $19^{\circ}$  C.

When the volume of water descending through the tower was less than 8 liters per minute (about 2.1 gallons), the concentration of the sulphur dioxide in the solution was close to that of theoretical saturation for water at those temperatures in equilibrium with the gas concentrations. The solubility of sulphur dioxide in water as given by Schönfeld<sup>a</sup> is taken as the basis for calculating the theoretical saturation concentration. For example, with an SO<sub>2</sub> content of 6.5 per cent in the gases in water at  $18^{\circ}$  C., a maximum concentration of about 7.4 grams per liter (0.99 ounce per gallon), was obtained, as against a theoretical saturation concentration of 7.8 grams per liter.

With an SO<sub>2</sub> content of 8.5 per cent in the gases the water solution at  $18^{\circ}$  C. contained 9.8 grams of SO<sub>2</sub> per liter, as against a maximum saturation concentration of 10.2 grams per liter.

However, in these tests in which nearly theoretically saturated solutions were obtained, not more than 50 per cent of the total SO<sub>2</sub> going to the towers was recovered. (See Table 1.)

By increasing the volume of water going through the tower to 11 liters per minute, about 70 per cent of the total SO<sub>2</sub> was recovered. The concentration of the SO<sub>2</sub> in the resulting solutions was within 80 per cent of that for the theoretical saturation. (See Table 1.)

In order to increase still further the total absorption of the sulphur dioxide, the volume of the solution descending through the tower was increased to as much as 16.5 liters (4.4 gallons) per minute. With this large volume of water the total absorption of the SO<sub>2</sub> was increased to as high as 90 per cent, but the concentration of the

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<sup>a</sup> Schönfeld, Franz, Ueber den Absorptions-coeffizienten der schwefligen Säure, des Chlors und des Schwefelwasserstoffs: Liebig's Ann., Bd. 95, 1855, p. 1; see also Landolt-Börnstein Physikalisch-Chemische Tabellen, 4th ed., 1212, p. 599.

sulphur dioxide in these solutions was in some cases as low as 70 per cent of that required for saturation. (See Table 1.)

Table 1 following gives a summary of the results of the tests.

TABLE 1.—*Summary of tests of absorption of sulphur dioxide in water.*<sup>a</sup>

[Dates of tests, Oct. 22–27, 1915.]

SOLUTION NEARLY SATURATED.

	Number of tests averaged.	Volume of gases to tower at 18° C. and 760 mm.	Temperature of gases at tower.	Per cent of SO <sub>2</sub> in gases to tower, average.	Weight of SO <sub>2</sub> to tower per minute, average.	Volume of water through tower, per minute.	Temperature of water at outlet.	SO <sub>2</sub> content of solution.		Percent of theoretical saturation.
								Per liter, average. <sup>b</sup>	Total per minute, average	
1915.		<i>Cu. ft.</i>	<i>°C.</i>		<i>Grams.</i>	<i>Liters.</i>	<i>°C.</i>	<i>Grams.</i>	<i>Grams.</i>	
Oct. 22.....	4	26	20	3.7	72.5	8.0	17	4.5	36.0	98
21.....	7	20	21	5.4	87.5	7.5	19	6.0	45.0	95
23.....	4	21	21	6.3	102.0	7.6	19	7.0	53.2	93
23.....	11	24	22	7.8	139.0	8.0	18	8.6	70.4	94
23.....	8	22	22	9.4	152.0	8.0	19	10.0	80.0	92

SOLUTION LESS SATURATED, BUT HIGHER PERCENTAGE OF SO<sub>2</sub> RECOVERED  
(APPROXIMATELY 70 PER CENT).

Oct. 22.....	5	25	20	3.5	68.6	12.0	17	4.0	48.0	91
27.....	8	22	22	6.0	97.2	11.0	18	6.2	68.3	86
23.....	3	21	21	7.0	113.5	11.0	18	7.1	78.2	84

UNSATURATED SOLUTION, RECOVERY OF SO<sub>2</sub> MORE NEARLY COMPLETE (APPROXIMATELY 85 PER CENT).

Oct. 22.....	5	21	22	5.2	84.2	16.2	17	4.8	77.8	74
22.....	4	21	20	6.5	105.2	15.5	17	5.7	88.5	71
27.....	9	22	21	7.2	116.8	15.0	18	6.1	91.6	71
27.....	3	21	22	8.1	131.0	16.0	18	7.0	112.0	72

<sup>a</sup> Tests by A. E. Wells, W. Freeman, R. Buhman, C. E. Brandt, and A. L. Tuttie.

<sup>b</sup> Grams per liter multiplied by 0.133=ounces per gallon.

ABSORPTION OF SULPHUR DIOXIDE IN MOTHER-LIQUOR SOLUTIONS.

The composition of mother liquor circulated through the tower to absorb the sulphur dioxide was not constant. The amount of barium in solution varied, according to the conditions under which the preceding precipitation had taken place, between 2 and 15 grams per liter. The ratio of sulphur to barium varied between 2 atoms of S to 1 atom of Ba, and 5+ atoms of S to 1 atom of Ba. These data, summarized briefly below, were obtained with a mother liquor having an average specific gravity of 1.035, a barium content of about 10 grams per liter, and a ratio of sulphur to barium of 3 to 5 atoms of S to 1 atom of Ba.

In determining the sulphur dioxide present in these solutions, samples were taken from the stream running out of the tower. These were titrated with a standard alkali, methyl orange being used as an

indicator. With methyl orange, neither the thiosulphate, the thiocyanates, nor the bisulphite that might be present in the solution was titrated, and the alkali used was equivalent only to one-half the free sulphur dioxide. In other samples the total iodine value of the sample was determined. The samples were then heated to 70° to 80° C. to drive off the sulphur dioxide, and the iodine equivalent of the thiosulphate or bisulphite was determined, this equivalent being deducted from the total iodine value.

In 56 tests, with the velocity of the gases through the tower averaging 2 feet per second, and with the sulphur dioxide content varying between 4.8 and 6.5 per cent, approximately 73 per cent of the total sulphur dioxide was recovered with an average volume of 9 liters (2.37 gallons) of solution per minute descending through the tower. The resulting concentrations of sulphur dioxide in the solutions averaged 20 per cent greater than those theoretically possible in pure water at the same temperature, and in equilibrium with the gas concentrations.

TABLE 2.—*Absorption of sulphur dioxide in mother liquor of Thiogen process, with SO<sub>2</sub> content of 4.8 to 6.5 per cent.<sup>a</sup>*

[Dates of tests, Oct. 11–Nov. 26, 1915.]

Number of tests.	Volume of gases to tower at 18° C. and 760 mm.	Temperature of gases.	Per cent of SO <sub>2</sub> in gases to tower, average.	Weight of SO <sub>2</sub> to tower per minute, average.	Volume of solution through tower per minute.	Temperature of solution at outlet.	SO <sub>2</sub> content of mother liquor.		Ratio of concentration percentage attained to theoretical saturation concentration in water
							Per cent of total SO <sub>2</sub> absorbed in mother liquor solution.	Total in solution.	
6.....	Cu. ft.	° C.	Grams.	Liters.	° C.	Grams.	Grams.		
6.....	20	21	5.4	82.0	8.0	20	7.4	59.2	72
8.....	23	20	5.1	89.0	4.1	15	8.6	35.2	40
6.....	25	19	5.0	94.8	10.0	18	7.2	72.0	76
10.....	26	17	4.8	94.3	11.2	17	7.2	80.6	85
4.....	28	18	6.0	127.0	8.2	17	9.0	73.8	58
4.....	26	17	6.3	123.0	11.7	20	8.65	101.0	82
4.....	26	18	4.8	94.3	10.2	22	6.6	67.4	72
4.....	23	19	5.5	96.0	10.0	15	8.9	89.0	93
4.....	23	19	6.5	113.0	7.8	17	11.2	87.4	77
6.....	23	19	6.5	113.0	10.0	22	8.0	80.0	71

<sup>a</sup> Tests by A. E. Wells, W. Freeman, C. E. Brandt, A. L. Tuttle, and R. Buhman.

Thirty-two tests were made with the sulphur dioxide content of the gases varying between 7 and 10 per cent, and the volume of solution used varying between 7.0 and 7.5 liters per minute. The sulphur dioxide concentration of these solutions averaged about 12 per cent greater than was theoretically possible in pure water.

Ten tests were made when the gas concentration varied between 11 and 13 per cent sulphur dioxide, the volume of mother liquor circulated being about 7.5 liters (2 gallons) per minute. In these solutions

the sulphur dioxide concentration was only about 8 per cent greater than that for water saturation under the same conditions.

TABLE 3.—Absorption of sulphur dioxide in mother liquor of Thiogen process,  $SO_2$  content of gases above 7 per cent.<sup>a</sup>

[Dates of tests, Jan. 29 and Feb. 1, 1916.]

Number of tests.	Per cent of $SO_2$ in gases.	Volume of solution used per minute.	Temperature of absorbing solution from tower.	$SO_2$ content of solution per liter.	Ratio of concentration attained to theoretical saturation concentration in water.
8.	7.1	7.2	23	7.6	107
3.	7.6	7.2	27	7.2	110
18.	7.9	7.5	22	9.2	111
4.	9.1	7.0	19	12.4	117
6.	9.5	7.2	23	10.9	115
6.	9.6	7.1	19	12.7	113
5.	9.7	7.1	23	11.0	b 113
4.	10.7	7.2	27	10.0	108
1.	12.4	7.0	24	12.4	104
1.	12.5	7.1	24	12.8	108
3.	12.8	7.0	28	11.8	110
1.	12.9	7.1	24	13.5	c 110
4.	15.2	7.1	27	13.3	100

<sup>a</sup> Tests by A. E. Wells, W. Freeman, V. P. Edwards, and R. Buhman. <sup>b</sup> Average=112. <sup>c</sup> Average=108.

It is, of course, hardly true that the solution factors obtained in the tests represented actual saturation. However, inasmuch as with pure water the theoretical maximum concentration within 10 per cent was obtained, it is safe to assume that under the same conditions the tests with the mother liquor gave results that came within that limit.

These figures are slightly lower, about 10 per cent, than those obtained in a small glass absorption tower by D. E. Fogg,<sup>a</sup> former engineer for the Thiogen Co., who found also a decrease in the absorption coefficient with the higher gas concentrations, similar to that found in these tests. A comparison of concentrations obtained at 18° C. is given below.

#### Comparison of concentrations obtained in absorption tests.

Per cent of $SO_2$ in gases.	$SO_2$ concentration per liter in mother liquor with a specific gravity of 1.03.	
	Tests by D. E. Fogg.	Bureau of Mines tests.
	Grams.	Grams.
5	8.0	7.2
6	9.4	8.7
7	10.7	9.7
8	11.8	10.9
9	13.0	12.1

The results of absorption tests indicate that by the use of mother liquor as the absorbing liquid the concentration of the sulphur dioxide

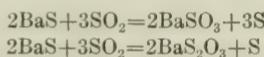
<sup>a</sup> Figures given in personal communication to author.

in the solution can be brought to at least that of a saturated solution of water under the same conditions and with the usual gas concentration found in practice the concentration will be 10 to 20 per cent higher than is theoretically possible in pure water. By the use of a tower of the same type and height as used in the experiments and with the gas velocity varying between 2.0 and 2.5 feet per second, these concentrations can be obtained simultaneously with the recovery of about 75 per cent of the sulphur dioxide in the gases.

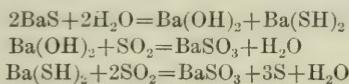
### **PRECIPITATION OF SULPHUR DIOXIDE AS BARIUM SULPHITE, THIOSULPHATE, AND SULPHUR.**

#### **OUTLINE OF TESTS.**

As stated above the reaction between barium sulphide and sulphur dioxide may be expressed as follows:



Barium sulphide in water solution is more or less hydrolyzed so that the solution contains  $\text{Ba}(\text{OH})_2 + \text{Ba}(\text{SH})_2$ . Thus a reaction between  $\text{BaS}$  in solution and  $\text{SO}_2$  solution may be written:



In this investigation it was necessary to determine the extent of these reactions under laboratory conditions and under the less completely controlled conditions likely to be met in large-scale operations. A knowledge of the physical characteristics of the precipitate formed under the different conditions was also essential.

Series of tests were made to determine the completeness of the reaction when the theoretical quantities were brought together (1) when both were in solution, (2) when the nearly pure solid barium sulphide was stirred into the sulphur dioxide solution, and (3) when the solid barium sulphide added was present in a reduced product of previous precipitations.

In other series similar precipitations were made when either barium sulphide or sulphur dioxide was present in excess.

In still other series repeated precipitations were made, the same mother liquor after filtration of the precipitate being used each time. The purpose of using the same mother liquor in the cycles was to determine the maximum concentration of barium salts that might be obtained in solution. These cyclic precipitations were first made on the small laboratory scale and later on the larger scale, when the barium compounds were used in cycles as well as the mother liquor.

The results of series of tests designated series A, B, C, and D, conducted on the small laboratory scale, are summarized below:

#### SERIES A PRECIPITATION TESTS.

In the Series A tests, standard solutions of barium sulphide were added at 20° C. to standard sulphur dioxide solutions in which there were no barium salts present.

The sulphur dioxide solutions were standardized against iodine and also against a standard alkali. The barium sulphide solutions were standardized against iodine and also by titration with a zinc hydroxide solution, nickel sulphate being used as an outside indicator.

Precipitations were made in glass-stoppered, wide-mouthed bottles, the solution being well shaken for several minutes during precipitation.

After the precipitate had been allowed to settle, an aliquot part of the solution was taken for the determination of excess uncombined sulphur dioxide. This was determined either by titrating with iodine both before and after the solution had been heated to 80° C., or by titrating with a standard alkali, methyl orange being used as an indicator. The precipitate was collected on a filter and washed once with hot water, and then dried at 100° C. Sulphur, barium sulphite, barium thiosulphate, and barium sulphate were then determined.

However, in some cases just the total acid soluble barium and insoluble barium were determined. Elemental sulphur was determined by leaching the precipitate with carbon bisulphide, evaporating off the carbon bisulphide on a tared watch glass, and weighing the residue sulphur.

As  $\text{Ba}(\text{OH})_2$  and  $\text{Ba}(\text{SH})_2$  are formed in dissolving BaS in water, it is necessary to keep the solution away from the atmosphere to prevent formation of the barium carbonate and loss of hydrogen sulphide. The sulphur dioxide solutions varied in strength from 0.66 gram to 37 grams of  $\text{SO}_2$  per liter. The amount of barium sulphide added was between 37 and 118 per cent of that theoretically necessary for the reaction.

In these tests when the amount of barium sulphide theoretically required was added, the sulphur dioxide was completely neutralized, no uncombined sulphur dioxide or barium sulphide remaining in the solution. When the sulphide was added in an amount less than that theoretically required for the reaction, the excess uncombined sulphur dioxide in the solution was always less than the theoretical excess. This was due to the fact that the excess sulphur dioxide, to a certain extent, reacted with the precipitated barium sulphite,

or thiosulphate, dissolving these as a thionate or sulphite in which the atomic ratio of S to Ba was greater than 2:1. The higher the concentration of the sulphur dioxide in the solution before precipitation, the greater is the concentration of these barium salts in solution, as is indicated by the results of tests B-7, E-2, C-1, B-2, E-3, C-5, and C-9 given in Table 4 following. Also the greater the amount of sulphur dioxide in excess over that required for the reaction with barium sulphide, the greater is the concentration of the barium salts and the greater is the ratio of the sulphur to the barium in the solutions.

When an excess of barium sulphide was added, the iodine titration of the solution after precipitation was equivalent to more barium sulphide than the calculated excess. This excess iodine value was due to the fact that the solution contained a greater proportion of the SH ions than the OH ions. In several cases where there was only a slight excess of barium sulphide added, the addition of sulphur dioxide in an amount equivalent to the iodine value was sufficient to neutralize the solution. In the second precipitation, in which the solution was neutralized with sulphur dioxide, or a slight excess of sulphur dioxide was added, the precipitate contained more sulphur in proportion to the barium than did the first precipitate, which also indicated the presence of excess SH ions, after the first precipitation.

Irrespective of the concentrations of the sulphur dioxide or the barium sulphide solutions, the precipitates in all cases were principally the barium thiosulphate and sulphur ( $2\text{BaS}_2\text{O}_3$  and S) with some barium sulphite and sulphur ( $2\text{BaSO}_3 + 3\text{S}$ ). In some precipitates the sulphate was found, owing no doubt to oxidation during filtration and drying.

The thiosulphate and the sulphite were slightly soluble, the amount going into solution varying according to the original sulphur dioxide content of the solution, and the excess sulphur dioxide remaining in solution after reaction.

The precipitates were mostly flaky and flocculent, some of them containing a much smaller proportion of a crystalline precipitate. This crystalline precipitate was the sulphite.

When the sulphur dioxide solution was completely neutralized, or when the solution contained an excess of sulphur dioxide, the precipitate settled very rapidly. In a solution that was alkaline owing to an excess of sulphide, the precipitate settled very slowly, having colloidal characteristics.

TABLE 4.—*Results of Series A precipitation tests.<sup>a</sup>***BARIUM SULPHIDE IN SOLUTION ADDED TO SULPHUR DIOXIDE SOLUTION.**

SULPHUR DIOXIDE SOLUTION, 36.8 GRAMS PER LITER; BARIUM SULPHIDE SOLUTION, 59.0 GRAMS PER LITER.

Test No.	Total SO <sub>2</sub> used.	Total BaS used.	Proportion of BaS referred to per centage theoretically required.	SO <sub>2</sub> per liter in solution after precipitation.		BaS per liter in solution after precipitation.		Ba per liter in solution.	Approximate atomic ratio S of Ba in solution.	Per cent of total Ba in solution.	Per cent of total Ba in precipitate.
				Theoretical.	Determined.	Theoretical.	BaS equivalent to I <sub>2</sub> titration.				
B-4.....	3.68	7.68	118	0.00	0.00	5.23	.....	5.26	2.5:1	20	80
B-3.....	3.68	6.84	105	.00	.00	1.71	2.85	4.63	2.2:1	18	82
B-7.....	3.68	6.48	100	.00	.00	.00	.00	2.99	2.0:1	12	88
B-8.....	3.35	5.90	100	.00	.00	.00	.00	2.64	2.0:1	11	89
B-2.....	3.68	5.90	91	1.65	.65	.00	.00	4.03	2.2:1	16	84
B-5.....	3.68	5.20	80	3.90	1.68	.00	.00	5.95	2.3:1	27	73
B-1.....	3.68	4.76	73	5.36	3.78	.00	.00	7.17	2.3:1	33	67
B-8.....	3.68	3.56	55	10.3	8.93	.00	.00	8.96	2.5:1	50	50

SULPHUR DIOXIDE SOLUTION, 18.0 GRAMS PER LITER; BARIUM SULPHIDE SOLUTION, 31.7 GRAMS PER LITER.

E-1.....	1.80	3.49	110	0.00	0.00	1.52	2.10	3.90	2.3:1	29	71
E-2.....	1.80	3.17	100	.00	.00	.00	.00	2.10	2.0:1	16	84
E-3.....	1.80	2.85	90	.95	.90	.00	.00	2.95	2.2:1	24	76
E-4.....	1.80	2.54	80	2.00	1.55	.00	.00	3.75	2.3:1	34	66
E-5.....	1.80	2.22	70	3.18	2.28	.00	.00	5.10	2.3:1	48	52

SULPHUR DIOXIDE SOLUTION, 4.4 GRAMS PER LITER; BARIUM SULPHIDE SOLUTION, 12.3 GRAMS PER LITER.

C-4.....	0.88	1.72	112	0.00	0.00	0.53	0.90	0.96	2.2:1	15	85
C-1.....	.88	1.54	100	.00	.06	.00	.00	1.40	2.0:1	34	66
C-5.....	.88	1.35	88	.35	.31	.00	.00	1.82	2.3:1	48	52
C-2.....	.88	1.23	80	.57	.56	.00	.00	1.84	2.3:1	55	45
C-6.....	.88	.96	62	1.19	1.12	.00	.00	1.75	2.3:1	59	41
C-3.....	.88	.80	52	1.58	1.43	.00	.00	1.50	2.4:1	58	42
C-7.....	.88	.57	37	2.91	2.20	.00	.00	1.20	2.4:1	98	2

SULPHUR DIOXIDE SOLUTION, 0.7 TO 1.5 GRAMS PER LITER; BARIUM SULPHIDE SOLUTION, 12.3 GRAMS PER LITER.

C-8.....	0.15	0.21	80	0.45	0.42	0.00	0.00	0.46	2.0:1	32	68
C-11.....	.15	.185	70	.70	.59	.00	.00	.65	2.0:1	50	50
C-9.....	.066	.104	90	.062	.060	.00	.00	.28	2.0:1	36	64
C-10.....	.070	.099	80	.130	.100	.00	.00	.24	2.1:1	32	68
C-12.....	.070	.086	70	.197	.145	.00	.00	.32	2.1:1	49	51

<sup>a</sup> Tests by A. E. Wells, W. Freeman, R. Buhman, C. E. Brandt, and V. P. Edwardes.**SERIES B PRECIPITATION TESTS.**

In the Series B tests, powdered barium sulphide was added to the sulphur dioxide solution which contained no barium salts. When powdered barium sulphide was used for precipitation, the precipitate always was mostly the thiosulphate and sulphur ( $2 \text{ BaS}_2\text{O}_3 + \text{S}$ );

but the SO<sub>2</sub> consumption per unit of BaS added was variable, depending to a great extent on the degree of fineness to which the barium sulphide had been pulverized, and on the rapidity with which the sulphide was stirred into the solution. Very often the free sulphur dioxide would be completely removed from solution before all the sulphide had dissolved, even when only 80 per cent of the theoretically required amount of the sulphide had been added, and later as this sulphide dissolved, the solution became alkaline.

In Table 5 following are given the data obtained in tests when barium sulphide (95 per cent BaS and 5 per cent BaSO<sub>3</sub>+BaSO<sub>4</sub>) pulverized to 200 mesh was used as the precipitant. The solid material was incorporated into the solution by vigorous shaking in a bottle.

TABLE 5.—*Results of Series B precipitation tests.<sup>a</sup>*

[Solid barium sulphide (95 per cent BaS, 200 mesh) added to sulphur dioxide solution, which before precipitation contained no barium salts.]

Test No.	SO <sub>2</sub> in solution per liter.	BaS added, per cent of theoretical required.	Excess SO <sub>2</sub> per liter.		Ba per liter in solution after precipitation.	Atomic ratio of S to Ba in solution.
			Calculated.	Determined.		
1.....	Grams.	Grams.	Grams.	Grams.	Grams.	
1.....	36.8	100	b 0.0	b 0.0	4.25	1.6:1
2.....	36.8	90	3.7	2.5	5.10	2.5:1
3.....	36.8	80	7.4	5.1	6.85	3.2:1
4.....	36.8	70	11.1	7.8	9.15	4.5:1
5.....	18.0	100	b .0	b .0	3.56	1.8:1
6.....	18.0	90	1.8	.0	3.95	3.1:1
7.....	18.0	80	3.6	1.9	4.50	3.2:1
8.....	18.0	70	5.4	2.8	5.80	3.5:1
9.....	7.3	100	b .0	b .0	1.26	1.8:1
10.....	7.3	88	.88	.30	1.62	2.2:1
11.....	7.3	43	4.16	2.20	4.10	3.5:1
12.....	4.4	100	b .0	b .0	1.15	1.9:1
13.....	4.4	90	.44	.00	1.50	2.2:1
14.....	4.4	80	.88	.30	1.60	2.3:1
15.....	.7	100	b .0	b .00	.60	2.0:1
16.....	.7	80	.14	.05	.95	2.0:1

<sup>a</sup> Tests by A. E. Wells, W. Freeman, R. Buhman, C. E. Brandt, and V. P. Edwards.

<sup>b</sup> Solution contained excess BaS.

Table 6 following gives a brief summary of the results obtained from two series of precipitations made by shaking in a bottle reduced barium sulphate containing 70 per cent barium sulphide with sulphur dioxide solution. In the first series the material was pulverized to 100 mesh, and in the second was pulverized only to 60 mesh.

The other 30 per cent of this reduced material was barium oxide, barium carbonate, barium sulphate, and coke ash. Special tests showed that both the oxide and the carbonate reacted very slowly with the dilute sulphur dioxide solution and hence could not account for the rapid elimination of sulphur dioxide from the solution.

TABLE 6.—*Results of precipitation tests<sup>a</sup> in which barium sulphide (70 per cent BaS, 100 or 60 mesh) was added to sulphur dioxide solution containing no barium salts.*

Test No.	SO <sub>2</sub> per liter in solution at start.	BaS added, per cent of theoretical required.	SO <sub>2</sub> per liter in solution at end.		Ba per liter in solution.	Atomic ratio of S in Ba in solution.	Remarks.
			Calculated.	Determined.			
1-0.....	Grams. 9.0	100	Grams. 0.00	b 0.00	1.52	1.9 : 1	
1-1.....	9.0	93	.63	.00	1.56	2.2 : 1	
1-2.....	9.0	83	1.53	.00	2.19	2.65 : 1	Material used 70 per cent. BaS, ground to 100 mesh.
1-3.....	9.0	72	2.51	.00	2.91	3.12 : 1	
1-4.....	9.0	62	3.42	.60	3.69	3.02 : 1	
1-5.....	9.0	52	4.32	1.52	4.06	3.10 : 1	
2-1.....	10.1	100	.00	b .00	(c)	(c)	
2-2.....	10.1	96	.40	b .00	(c)	(c)	
2-3.....	10.1	85	1.50	.00	2.98	2.3 : 1	
2-4.....	10.1	65	3.53	.00	4.80	3.0 : 1	
2-5.....	10.1	53	4.75	.15	6.11	3.1 : 1	

<sup>a</sup> Tests by A. E. Wells, W. Freeman, R. Buhman, C. E. Brandt, and V. P. Edwardes.

<sup>b</sup> Solution contained excess BaS.

<sup>c</sup> Not determined.

### SERIES C PRECIPITATION TESTS.

In the Series C tests, powdered barium sulphide was added to sulphur dioxide solution which contained barium salts before precipitation. The results of these tests can be summarized briefly by stating that when the sulphur dioxide solution contained originally some barium salts, the tendency for the free sulphur dioxide in the solution to react immediately with the first products of the reaction and to dissolve them was decidedly less than when the barium sulphide was added to a "straight" sulphur dioxide solution containing no barium salts.

The tendency for the removal of the sulphur dioxide from the solution by a reaction with the first precipitation products was less as the barium concentration in the solution was greater.

With a barium concentration of about 10 grams per liter, and the ratio of sulphur to barium in solution being 3 to 4 atoms of S to 1 atom of Ba, the reaction between barium sulphide and sulphur dioxide took place nearly according to the theoretical reaction, requiring 2 molecules of BaS to 3 molecules of SO<sub>2</sub>.

Unless there was considerable excess sulphur dioxide in the solution, the barium sulphide added reacted only with the theoretical amount of sulphur dioxide to form thiosulphate and sulphur (2BaS<sub>2</sub>O<sub>3</sub>+S). However, with considerable excess sulphur dioxide after the sulphide had dissolved, or with strong sulphur dioxide solution before precipitation, there was a tendency for the resolution of some of the precipitated barium salts and the formation of soluble thionates or sulphites.

### SERIES D PRECIPITATION TESTS.

In the Series D tests, repeated precipitations were made, the same solutions being used throughout a test. This series was in fact only a continuation of Series C, carried out with a sufficient number of repeated precipitations to indicate to what extent the barium salts would accumulate in the solution.

The precipitations were made from solutions of about 2 liters in volume.

In one set of tests, practically the theoretically required amount of barium sulphide was added each time. The amount of barium in solution increased as the number of precipitations until a maximum content of about 15 grams of barium per liter of solution was obtained. The ratio of barium to sulphur in solution at this point was approximately four atoms of sulphur to one atom of barium. The specific gravity of the solution was 1.045. This solution was allowed to stand for several days, when there was a crystallization of some of the barium salts, principally the thiosulphate.

Other series of cycles were run in which at certain precipitations insufficient barium sulphide was added, and at other precipitations the sulphide was added in excess. In these series, the barium content of the solution after precipitation was greater or less according to whether considerable excess sulphur dioxide was in the solution after precipitation, and according to the rapidity with which the material was stirred into the solutions.

In these laboratory cycle series the barium content of the solution never went above 18 grams per liter, and the ratio of sulphur to barium never went above 5 atoms of S to 1 atom of Ba.

The specific gravity of these solutions never exceeded 1.05. Table 7 following shows the results of two tests, which are given as examples of the data obtained from several tests.

TABLE 7.—*Results of Series D precipitation tests.<sup>a</sup>*

[Repeated precipitations.]

TEST 1.

Precipitate No.	SO <sub>2</sub> per liter in solution at start.	BaS added, per cent of theoretical required.	SO <sub>2</sub> per liter in solution at end.		Ba per liter in solution.	Ratio of S to Ba in solution.	Specific gravity of solution.
			Calculated.	Determined.			
1	9.2	100	0	(b)	2.25	1.6:1	1.010
2	10.0	100	0	(b)	3.90	2.2:1	(c)
3	10.0	100	0	(b)	5.88	3.0:1	(c)
4	9.3	100	0	0.0	6.76	3.4:1	1.020
5	9.0	100	0	.2	8.10	4.0:1	(c)
6	10.1	100	0	.5	9.45	4.5:1	(c)
7	9.5	100	0	.2	12.20	(c)	1.040
8	11.5	100	0	.0	13.40	5.1:1	(c)
9	9.5	100	0	.2	15.50	(c)	1.040
10	11.5	100	0	.0	14.20	4.7:1	(c)
11	10.2	100	0	.2	14.80	(c)	(c)
12	9.5	100	0	.1	15.25	(c)	1.045

TEST 2.

1	9.6	50	4.8	2.3	5.50	3.1:1	1.015
2	10.2	100	0	(b)	4.80	3.0:1	(c)
3	9.5	80	1.9	.0	8.22	3.5:1	(c)
4	11.5	95	.6	.0	9.00	3.8:1	(c)
5	9.5	80	1.9	.8	8.10	4.1:1	1.020
6	11.4	118	0	(b)	7.15	4.0:1	(c)
7	9.0	140	0	(b)	6.90	4.0:1	(c)
8	10.2	60	4.3	3.2	10.10	4.5:1	(c)
9	11.2	100	0	.0	9.15	4.5:1	(c)
10	11.2	100	0	.0	9.85	4.5:1	1.030

<sup>a</sup> Tests by A. E. Wells, W. Freeman, R. Buhman, C. E. Brandt, and V. P. Edwardes.

<sup>b</sup> Excess BaS.  
<sup>c</sup> Not determined.

### SUMMARY OF RESULTS OF TESTS IN SERIES A TO D.

The small-scale laboratory tests embraced in series A to D indicated that the main reaction between barium sulphide and sulphur dioxide was  $2\text{BaS} + 3\text{SO}_2 = 2\text{BaS}_2\text{O}_3 + \text{S}$ . The thiosulphate and sulphur were the main part of the precipitate, whether the sulphide was added in solution or in finely powdered form.

When solution was added to solution in nearly equivalent amounts there was only a slight tendency for complex soluble thionates, or sulphites, to form, although a small percentage of the thiosulphate dissolved in the mother liquor.

When solid barium sulphide was added to the sulphur dioxide solution, unless the solution already contained between 10 and 15 grams of barium per liter, the  $\text{SO}_2$  equivalent per unit of  $\text{BaS}$  was greater than the theoretical, this excess sulphur dioxide consumption being due to the sulphur dioxide reacting with the barium sulphite, or to the thiosulphate being precipitated to form complex soluble thionates or soluble sulphites. This tendency, however, would not be a serious factor in practical work, as the concentration of the barium salts remained comparatively low and the maximum specific gravity of the solution was about 1.05.

In the tests it was noted that the settling of the precipitate was most rapid when the solution was nearly neutral after precipitation and when the specific gravity of the solution was about 1.03.

### LARGE-SCALE PRECIPITATIONS.

The large-scale precipitations were made with the apparatus shown in Plate I, A (p. 10).

Sulphur dioxide from the furnace gases was absorbed in the tower by the mother liquor, which was pumped to the top of the tower and ran out at the bottom into the tubs, which held 70 liters (18.5 gallons) of solution. The sulphur dioxide content of the solution was determined immediately after a tub had been filled, and then a weighed amount of a product from the reduction process, containing barium sulphide, was incorporated into the solution by vigorous stirring and agitation. This stirring was done by hand with a paddle for a period of 5 to 10 minutes. The precipitate, in most cases practically all  $2\text{BaS}_2\text{O}_3 + \text{S}$ , was allowed to settle, and the mother liquor was then siphoned off by a pump and lifted to the top of the tower for the absorption of more sulphur dioxide.

The precipitate was filtered and dried, and the sulphur was distilled from it. After distillation of the sulphur, the residue ( $\text{BaSO}_3 + \text{BaSO}_4$ ) was mixed with pulverized coke and reduced in a furnace to the sulphide. Thus, in these tests not only was the mother liquor used in cycles but the barium compounds were used repeatedly.

In the first cycles, the sulphur dioxide consumption factor per unit of reduced material was a variable, as in the small laboratory-scale precipitation. After several cycles of the mother liquor, when the barium content of the solution had been built up to 8 to 10 grams per liter, the sulphur dioxide consumption factor of the reduced material became more constant. The addition of an insufficient amount of the reduced material to take care of the sulphur dioxide according to the reaction  $2\text{BaS} + 3\text{SO}_2$  resulted simply in the presence of excess sulphur dioxide after precipitation. The barium content of the mother liquor was about 8 grams per liter when the solution was nearly neutral after precipitation, but was as high as 12 grams per liter when considerable excess sulphur dioxide was present.

When the products of reduction of previous precipitates were used, especially after the barium compounds had been carried through several cycles, it was rather difficult to calculate from analysis the exact sulphur dioxide equivalent per unit of reduced product. The factor had to be determined by trial, an approximate calculated factor being used at the start. This was due to the fact that most reduction products contained barium oxide and barium carbonate, especially after the first few cycles, when the reductions were effected in a direct-fired furnace. Some of the oxide was readily soluble in water, and this reacted readily in the sulphur dioxide solution, forming the sulphite. However, a considerable part of the oxide was slowly soluble. In some products a small proportion of the sulphide was nearly insoluble.

The slowly soluble compounds in the reduced product reacted slowly with the sulphur dioxide solutions, especially with the dilute solution remaining after the greater part of the sulphur dioxide had been removed by the readily soluble barium sulphide. Most of the nearly insoluble barium oxide was so insoluble that the first part to go into the solution frequently reacted with the excess sulphur dioxide to form a soluble bisulphite, removing the free sulphur dioxide before the rest of the barium oxide dissolved.

However, when trial had shown the sulphur dioxide equivalent of the reduced product under the conditions for precipitation, there was no difficulty experienced in causing the sulphur dioxide to be completely precipitated from the solution and in keeping the barium content of the solution down to less than 10 grams of barium per liter. For example, in one series, the mother liquor was used throughout 58 cycles. At the end the solution contained 7.6 grams of barium per liter, the ratio of sulphur to barium being equal to 5.8:1 and the specific gravity of the solution being 1.032.

The ratio of sulphur to barium in the mother liquor at times was as high as 7 atoms of sulphur to 1 atom of barium. Some attempts were made to determine the exact composition of the barium salts in

solution by causing crystallization of these salts. However, they were unstable, and every attempt to evaporate the solution by heating resulted in the precipitation of sulphur and barium sulphate, and in some tests in the evolution of sulphur dioxide.

Rhombohedral crystals were obtained by cooling the solution to a temperature slightly below that of precipitation. These crystals contained 2 atoms of sulphur to 1 atom of barium, corresponding to the thiosulphate  $\text{BaS}_2\text{O}_3$ , or to the barium dithionate  $\text{BaS}_2\text{O}_6$ .

In these large-scale precipitations, it was noted that considerable heat was liberated in the reactions between the solid barium sulphide and the sulphur dioxide. Thus, for example, 70 liters of solution containing 9.8 grams of  $\text{SO}_2$  per liter, or a total of 0.680 kilogram  $\text{SO}_2$ , was precipitated with 1.7 kilograms of reduced material containing 70 per cent (1.20 kilograms) of  $\text{BaS}$ . The rise in temperature of the solution was  $2.5^\circ \text{C}$ . ( $30.5^\circ$ – $28^\circ \text{C}$ .). The approximate heat liberated was 175 kilogram calories, or 103 kilogram calories per kilogram of reduced material.

#### PRACTICAL CONSIDERATIONS REGARDING PRECIPITATION.

In practice the precipitant will have to be incorporated mechanically with the solution as the latter runs into the agitating tank. This can be done, as planned by the Thiogen Co., by pumping a part of the solution containing the sulphur dioxide through an incorporator with an adjustable feed, and then mixing the emulsion and the rest of the solution through a centrifugal pump discharging into an agitator. A skilled attendant will be required to regulate the feed of precipitant to meet the sulphur dioxide content of the solution. The precipitant will probably have to be used in large batches of fairly constant composition and sulphur dioxide combining value, so that the regulation of feed can be adjusted without much difficulty.

The heat generated in the precipitation is of some practical importance, as this heat must be removed either in the settling tank, or in the storage tanks; otherwise the solution will become so warm that its absorbent efficiency will be greatly decreased.

#### SETTLING PRECIPITATE AND DECANTING MOTHER LIQUOR.

For practical use the data obtained on the settling of the precipitate in the large-scale precipitations in the tubs are much more valuable than those obtained in the small-scale laboratory experiments. However, the small-scale experiments indicated that settling took place most rapidly from a nearly neutral solution, and was slowest from a solution containing excess barium sulphide, that is, an alkaline solution.

In the large-scale work the precipitations were made about as follows: Five tubs of 70-liter capacity each were used for precipitation

and settling. Each tub was filled in 7 to 10 minutes with the mother liquor containing sulphur dioxide running from the towers. The analyses for sulphur dioxide in the solution and the weighing of the reduced material for precipitation took about two minutes. The solid precipitate was then stirred vigorously into the solution for 6 to 8 minutes until the next tub following was nearly filled. Generally, this tub was again stirred for several minutes until the second following tub was nearly filled and was then allowed to settle. By the time the mother liquor of this tub had to be drawn for return to the towers, about 15 or 20 minutes later, the precipitate had almost completely settled, leaving a supernatant liquor in which there were some flakes of sulphur floating.

Thus, in these tests, a settling capacity equivalent to the volume of solution coming from the towers in 20 minutes was ample to allow satisfactory settling.

When the precipitation was carried out properly, that is, when the solid precipitant was stirred vigorously into the solution and the solution after precipitation was nearly neutral, about 90 per cent of the precipitant settled 12 inches to the bottom of the tub within three minutes. This settling was even more rapid after a precipitation in which a considerable part of the solid material added did not react with the sulphur dioxide in the solution, that is, was comparatively insoluble.

The supernatant liquor after settling 10 minutes still contained some light, flaky precipitate, largely sulphur, in most cases less than 1 per cent of the total. This could be handled without any difficulty through the gear pumps, centrifugal pump, or plunger pump used at different times. This light precipitate did not settle in the absorption tower, nor did the amount in the mother liquor increase markedly, unless, as stated above, the solution became alkaline.

The mother liquor could be drained off to the point where the residual precipitated sludge contained not over 50 per cent water.

#### FILTRATION OR DEWATERING OF PRECIPITATE.

In most of the large-scale tests the precipitated sludge was washed or shoveled from the precipitation or settling tubs onto a canvas filter of about 0.279 square meter (3 square feet) area, under which there was maintained a vacuum of about 38 centimeters (18 inches) of mercury. Without a vacuum a cake about 1 centimeter ( $\frac{3}{8}$  inch) thick was obtained in 10 minutes. With vacuum a 4-centimeter (1 $\frac{1}{2}$ -inch) cake could be dewatered in 2 minutes, only about 25 per cent water being left in the cake. With a 38-centimeter vacuum, a 5-centimeter (2-inch) cake could be obtained easily.

It was found that the precipitate when once settled should be separated from the supernatant liquor and filtered within a few

hours. In several tests the precipitated sludge was allowed to stand 24 to 48 hours in contact with a neutral mother liquor solution. As a result the precipitate became colloidal and slimy and offered serious obstacles to filtration. One particular lot of precipitated sludge had stood in contact with the mother liquor for 24 hours. After decantation it contained 65 per cent water and 35 per cent solids. An attempt to filter this through a Merrill dry discharge press, with a filtering area of 9 square feet and under an air pressure of 30 to 35 pounds, gave only a  $\frac{3}{8}$ -inch cake in  $1\frac{1}{2}$  hours, the resultant cake containing 45 per cent water.

However, when the sludge was filtered soon after it had settled no difficulties whatever were experienced in the operation. The water content of the cake was reduced to as low as 18 per cent in several tests when air was drawn through the cake for 4 to 5 minutes after the greater part of the water had been removed. An average cake contained 20 to 26 per cent moisture.

In the dewatering as in the filtering operations, the rapidity was greater in the case of precipitated sludge containing other barium compounds than the precipitate; that is, the barium compounds that did not react with the sulphur dioxide.

The conclusions from all the work on filtering the precipitate were that if filtration was accomplished soon after settling no difficulty should be experienced in reducing the moisture to about 25 per cent. Standard dewatering apparatus, for example, an Oliver filter or a Merrill or a Kelly press, would be satisfactory.

#### DRYING PRECIPITATE.

A drying plate having an area of about 7.5 square meters (25 square feet) was built of 1-centimeter ( $\frac{3}{8}$ -inch) iron plates. These plates were placed about 2.5 centimeters (5 inches) above the floor and gas burned beneath. The sides of this drying oven were of brick. The precipitate was stirred frequently and evaporation was assisted by blowing air over the surface. It was necessary to prevent the material from getting too hot locally, for in that event the sulphur started to distill and burn. It was noted that there was a slight distillation of sulphur even at  $110^{\circ}\text{ C}$ .

In the product from this dry plate 6 to 25 per cent of the total barium was present as sulphite, 40 to 85 per cent as thiosulphate, and 7 to 34 per cent as sulphate. The product contained 6 to 10 per cent elemental sulphur. It was not necessary to regrind the dried precipitate before distillation.

In practice, drying would undoubtedly be best accomplished by steam coils, or by a special type of muffle furnace in which there would be no danger of local overheating, with attendant loss of sulphur.

**DISTILLATION AND RECOVERY OF SULPHUR.**

In the tests it was determined that by heating the dried precipitate in a retort to 450° to 460° C. all the elemental sulphur as well as one-half the sulphur in the barium thiosulphate could be distilled.

Only in the small laboratory experiments was the sulphur distilled and condensed under such conditions that the sulphur was completely recovered and a quantitative sulphur balance obtained.

In the laboratory tests distillations were effected in glass retorts placed in an electrically heated furnace and the sulphur was recovered in glass condensers. In most cases there was a slow stream of nitrogen or sulphur dioxide passed through the retort into the condenser to remove the sulphur vapors.

In the distillation tests the sulphur began to distill rapidly at 180° C., and from that temperature up to 450° C., the boiling point of sulphur, the rate of distillation depended on the temperature and the rapidity with which the vapors were removed from the retort.

In all cases, whether the precipitate was almost entirely (2BaS<sub>2</sub>O<sub>3</sub>+S) or whether considerable (2BaSO<sub>3</sub>+3S) was also present, the sulphur was rapidly and completely distilled at 450° C. The condensed sulphur was practically pure.

The residual product from the distillation was barium sulphite, sulphate, and in some cases a small amount of sulphide. Even when special care was taken to exclude air from the retort there was some slight oxidation of the sulphite to sulphate. Sometimes, when air was not completely removed or when air could get in contact with the hot residue after removal of the sulphur vapors, considerable sulphate formed.

Also, when the material was heated to a temperature higher than 450° C. there was some conversion of the sulphite to sulphide and sulphate according to the equation: 4BaSO<sub>3</sub>=BaS+3BaSO<sub>4</sub>. In one product from a distillation at 600° C., 6 per cent of the barium was present as sulphide.

In the large-scale experiments, different methods for the distillation and condensation of the sulphur vapors were tried in a rough way, but no apparatus was built that gave complete recovery of the sulphur. Flowers of sulphur, or rubber-like modifications were obtained according as the vapors were allowed to condense slowly, or cooled quickly by precipitation on chilled surfaces. A discussion of the various methods used is not considered necessary as giving any data worth recording.

In order to effect a rapid distillation of the sulphur, the mass had to be stirred or agitated. Besides allowing the vapors to escape readily, the agitation prevented the mass from balling or caking.

Most distillations were condensed in an iron kettle placed in a brick furnace fired by gas. The temperature was measured in the mass

being distilled. By allowing sulphur vapors to burn a short distance above the material under treatment, the material was kept out of contact with the air. Other distillations were made in a 6-inch iron pipe, which was rapidly revolved in a brick furnace. In these distillations the sulphur vapors were condensed in an iron cylinder. The residual products were barium sulphite and sulphate, no thiosulphate being present. In the products of the cyclic operations there was also the oxide and the carbonate that had not reacted with the sulphur dioxide.

Some of the products contained as much as 50 per cent of the barium as sulphate; others only about 10 per cent. In practical operations it would probably be safe to figure that 30 to 40 per cent of the barium in the product would be present as sulphate, and the rest as sulphite, except 2 or 3 per cent as sulphide.

The product was pulverized, and was readily mixed with pulverized coke for the subsequent reduction.

The tests indicated that in practice the distillation of the sulphur from the dried precipitate consisting of either  $(2\text{BaS}_2\text{O}_3 + \text{S})$  or  $(2\text{BaSO}_3 + 3\text{S})$  should give no difficulty. Necessarily, the furnace for distillation must be heated externally and be provided with apparatus for stirring the charge. For quickly removing the sulphur vapors from the distillation furnace, it would be advisable to keep a current of sulphur dioxide gas circulating through the distillation furnace into the condensation chamber.

#### REDUCTION.

Reduction of the barium sulphite and the barium sulphate was recognized at the beginning of the study of the Thiogen process, as being probably the most important factor in the whole process.

In answer to several inquiries concerning what was being accomplished at the present time in the reduction of barium sulphate at various plants where barium salts were being manufactured from barium sulphate, the information was gained that although 80 or 85 per cent of the barium was readily reduced to acid-soluble compounds, yet current practices rarely reduced more than 60 or 70 per cent of the barium to water-soluble barium sulphide.

Information gained from the literature <sup>a</sup> showed that it was difficult to reduce more than 80 per cent of the barium to the sulphide, and that a 70 per cent reduction was more often the best result obtained in practice.

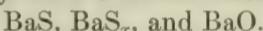
In order that the barium shall be efficient as a precipitant during the Thiogen process cycles, the maximum reduction of the sulphite

<sup>a</sup> Frazier, Schuyler, Calcining plant for barium sulphate: Min. Ind., vol. 19, pp. 71-73; Fay, A. N., Roasting barytes: Min. Ind., vol. 19, pp. 73-75; Toch, Maximilian, The barium industry in the United States since the European War: Met. and Chem. Eng., vol. 14, January, 1916, pp. 47-49.

or the sulphate to the water-soluble sulphide must be attained in each cycle. Thus, it was necessary to determine the conditions under which the barium sulphite or sulphate was reduced most completely to the sulphide, and considerable experimental work has been conducted on that problem. As barium sulphate must be used at the start in the initial reduction, and was present to a large extent in all precipitates after distillation, and also as this material could be obtained in quantities much more readily than the sulphite, the greater part of the investigations dealt with the reduction of the sulphate.

Before beginning the discussion of the several series of reduction tests, it is advisable to discuss briefly the character of the products obtained, and the manner in which these products are classified in this discussion. The barium compounds found in the reduced products were as follows:

1. Compounds readily soluble in hot water—



2. Compounds difficultly soluble in hot water but readily soluble in dilute hydrochloric acid—



3. Compounds insoluble in acid—



#### DETERMINATION OF WATER-SOLUBLE BARIUM.

The reduced product, ground to 100-mesh, was leached in a flask with 250 parts of water, which was just below the boiling point and filtered into a flask which was tightly stoppered while the solution was cooling. An aliquot part of the solution was then titrated with iodine, and in another aliquot part, barium and sulphur were determined. As a check for the iodine value, that is, the barium sulphide content, the material was frequently treated directly in a flask with excess iodine for about five minutes, and then the excess iodine was determined. In many cases excess barium hydroxide was present in the water solution. In other products there was a slight excess of sulphur over that required for the barium to form sulphide, indicating a polysulphide. In several products of reductions at high temperatures, 1050° to 1200° C., and in which excess carbon was present, the presence of the carbide was indicated, but was not determined quantitatively.

#### BARIUM COMPOUNDS SLOWLY SOLUBLE OR INSOLUBLE IN HOT WATER, BUT READILY SOLUBLE IN DILUTE ACID.

In many products from the first reduction, a large part of the oxide present was slowly soluble in hot water, but was readily soluble in dilute hydrochloric acid.

In most of the products of the reductions that were effected in a direct-fired furnace at high temperatures, and in which slight sintering had taken place, a small amount of the sulphide was found in the water-insoluble part. In some products 4 to 6 per cent of the total sulphide was found to be slowly soluble in water. The solubility of this material was increased somewhat by finer grinding. The insolubility of this part of the sulphide was due probably to its being covered with a film of the oxide. In a typical average product from the first reduction of barium sulphate 97 per cent of the sulphide and 40 per cent of the oxide was readily soluble in hot water, the rest being found in the acid-soluble part.

In this water-insoluble but acid-soluble part was also found the carbonate in varying amounts. The products from slow reductions at low temperatures contained more carbonate than did the products from rapid reductions at high temperatures.

Few products contained more than a trace of the sulphite or the thionates.

These insoluble barium products reacted very slowly with the sulphur dioxide in the dilute solutions. Thus, in certain cycles described later the proportion of these compounds increased to the point that over 40 per cent of the total barium was present in the form of soluble or insoluble oxide and insoluble carbonate. For example, as an extreme case, in the reduced product from the fourth cycle of one series of cyclic operations the barium compounds were found to be soluble to the extent shown below. These barium compounds were first pulverized to 100 mesh and then leached in a flask with 250 parts of hot water, subsequent leaching being made in a beaker.

*Results of leaching tests of barium compounds.<sup>a</sup>*

Material.	Barium compound.	Barium recovered, percentage of total barium content in original material.
A. Soluble products in solution obtained by leaching pulverized barium compounds with 250 parts of hot water for 15 minutes.....	(BaS).....	38.3
B. Soluble products obtained by leaching residue from A with 250 parts of hot water for 2 hours.....	(BaO).....	24.9
C. Soluble products obtained by leaching residue from B with boiling water for 10 hours.....	BaS + BaO.....	4.2
D. Soluble products obtained by leaching residue from C with boiling water for 12 hours.....	BaS + BaO.....	8.0
	BaS + BaO.....	6.2
Total soluble products from solutions B, C, and D (24 hours' leaching).....	(BaS).....	3.9
E. Soluble products obtained by leaching residue from D with dilute HCl.....	(BaO).....	14.5
F. Insoluble residue in dilute HCl solution (E).....	BaO, BaCO <sub>3</sub> and BaSiO <sub>3</sub> .....	8.6
	BaSO <sub>4</sub> .....	9.8

<sup>a</sup> Tests by R. Buhman and V. P. Edwardes.

### RESULTS OF REDUCTION TESTS.

The reduction tests were divided into five series, designated series 1 to 5, and the results are here considered under each series heading.

#### SERIES 1 TESTS.

In the Series 1 tests were embraced tests to determine the relative rates of reduction of barium sulphate by hydrogen, carbon monoxide, and a mixture of these gases with other hydrocarbons at different temperatures. In the tests precipitated barium sulphate (99+ per cent  $\text{BaSO}_4$ ) was placed in a quartz tube of about 12 mm. (0.47 inch) diameter, and heated in an electrically heated tube furnace. The barium sulphate was placed between two asbestos plugs, filling the tube for a distance of about 30 mm. (1.18 inches), but was sufficiently loose to allow the passage of gases through the material. The gases were passed through the tube at the rate of about 2 c. c. per minute. The temperature range was between  $600^\circ$  and  $1,050^\circ$  C. The data obtained probably did not represent the chemical equilibrium at any temperature. The comparative rate of reaction at different temperatures was obtained, however, as were data concerning the character of the gaseous products.

#### REDUCTION WITH HYDROGEN.

When hydrogen was used as the reducing agent there was practically no reaction at any temperature below  $550^\circ$  C. Around  $600^\circ$  C. the reaction was extremely slow, less than 5 per cent of the hydrogen that passed through the plug reacting. The gaseous product contained considerable hydrogen sulphide. At  $650^\circ$  C. about 15 per cent of the hydrogen reacted. At  $700^\circ$  C. about 35 per cent reacted. Between  $600^\circ$  and  $700^\circ$  C. the amount of hydrogen sulphide formed was a maximum. At  $800^\circ$  C. practically all the hydrogen had reacted and little hydrogen sulphide was present in the gaseous product. In general, these data checked those of a previous investigation.<sup>a</sup>

In the products from these reductions with hydrogen the ratio of sulphur to barium was less than one atom of sulphur to one atom of barium.

If the reductions were effected slowly at lower temperatures, that is, between  $600^\circ$  and  $750^\circ$  C., the loss of sulphur was greater than if the reductions were effected more rapidly at a higher temperature, as between  $900^\circ$  and  $1,000^\circ$  C. In one test lasting for an hour at  $1,000^\circ$  C. 94 per cent of the sulphate was reduced to sulphide and 6 per cent to oxide. This was the maximum reduction obtained with the use of hydrogen.

<sup>a</sup> Marino, I. L., [Technical preparation of barite]: Am. Chem. Soc. Abs., vol. 7, 1913, p. 3202; [Reduction of sulphate of alkaline earths with various gases]: Gazz. Chim. Ital., vol. 43, pp. 416-22

In some correlated tests it was found that between 700° and 900° C. water vapor reacts slowly with barium sulphide, forming sulphur dioxide, hydrogen sulphide, and barium oxide. For example, through a reduced product of about 20-mesh size, containing 89 per cent of the barium as sulphide, 7 per cent as oxide and carbonate, and 4 per cent as sulphate, was passed at 900° C. a mixture of about 16 per cent water vapor and 84 per cent nitrogen. About 1 per cent of the water vapor reacted, forming nearly two volumes of sulphur dioxide per volume of hydrogen sulphide. The reaction between water vapor and barium sulphide at other temperatures was not determined.

#### REDUCTION WITH CARBON MONOXIDE.

With carbon monoxide the reduction was slow below 650° C. and was fairly rapid at 750° C., about 70 per cent of the carbon monoxide reacting. With temperatures up to 900° C., however, there was present in the gaseous product some unconsumed carbon monoxide. Above that temperature the gaseous product was almost entirely carbon dioxide. In these reduced products the ratio of sulphur to barium was slightly less than 1 to 1, showing that some sulphur had been removed in the gaseous products.

In this series, as in tests with hydrogen as the reducing gas, the loss of sulphur was less when reduction was effected rapidly at higher temperatures, that is, above 900° C., than when effected slowly at lower temperatures. Thus the products of reduction effected rapidly at high temperatures contained the smaller percentages of water-insoluble barium oxide.

#### REDUCTIONS WITH CITY GAS.

In a series of 20 reductions an excess of city gas of approximately the following composition was passed at the rate of 2 c. c. per minute through the charge in the quartz tube:

*Composition of city gas used in reduction experiments.*

	Per cent.
Methane ( $\text{CH}_4$ ).....	6.4
Ethane ( $\text{C}_2\text{H}_6$ ).....	30.4
Hydrogen (H).....	41.4
Carbon monoxide (CO).....	13.4
Carbon dioxide ( $\text{CO}_2$ ).....	4.0
Nitrogen (N).....	4.2
Oxygen (O).....	.2

The results of the experiments are given in Table 8 following:

TABLE 8.—*Results of tests involving reduction of precipitated BaSO<sub>4</sub> by city gas in quartz tube, externally heated.<sup>a</sup>*

Temperature.	Time.	Per cent of total Ba in product present as—		
		Water-soluble BaS and BaO.	Water-insoluble, acid-soluble BaO and BaCO <sub>3</sub> .	Acid-insoluble BaSO <sub>4</sub> .
650–700	60	2.5	4.0	93.5
	240	58.0	15.8	26.2
	330	72.5	18.2	9.3
700–750	60	8.5	6.8	84.7
	240	75.0	13.8	11.2
750–800	60	20.6	8.4	71.0
	240	88.2	11.0	0.8
800–850	60	50.8	7.8	41.4
	240	91.5	8.3	0.2
850–900	60	55.5	6.8	37.7
	240	91.8	8.0	0.2
900–950	60	65.2	6.2	28.6
	120	85.0	7.3	7.7
	240	92.5	7.5	0.0
950–1,000	60	74.7	4.8	20.5
	120	91.5	6.5	2.0
	240	93.2	6.8	0.0
1,000–1,050	60	85.2	5.0	0.8
	120	92.0	6.5	1.5
	240	93.0	7.0	0.0

<sup>a</sup> Tests by W. Freeman, R. Buhman, C. E. Brandt, and V. P. Edwards.

The results presented in the preceding table indicate that in the tests in which city gas was used the percentage of barium in the product present in water-insoluble, acid-soluble compounds was less when reductions were effected in a short period of time at temperatures above 900° C. than if effected over a longer period of time at lower temperatures. For example, the products obtained when the material was treated for 330 minutes at 650° to 700° C. should be compared with the products obtained in a reduction at 1,000° to 1,050° C., lasting only 60 minutes.

It is also evident that any tendency for a reaction between the reducing gases and the sulphide, resulting in the formation of water-insoluble barium compounds, is slight. For example, the proportion of these compounds in the products of reductions at 900° to 1,050° C. for 60, 120, and 240 minutes should be compared.

#### SERIES 2 TESTS.

In the Series 2 tests barium sulphate was reduced by carbon. Finely pulverized carbon, either coke or charcoal, was intimately mixed with the barium sulphate and heated for varying periods of time at different temperatures in crucibles or tubes placed in muffle furnaces.

The theoretical amount of carbon required for the reduction is 10.3 per cent of the weight of BaSO<sub>4</sub> if the carbon is completely oxidized

to the dioxide, or is 20.6 per cent, if the carbon is oxidized only to the monoxide. In the tests the carbon added varied between 10 and 40 per cent of the  $\text{BaSO}_4$ .

The temperature range was between  $700^\circ$  and  $1,250^\circ \text{ C}$ . The time allowed for reduction varied between 15 and 360 minutes.

In all but a few of the tests, in which the time allowed for reduction was an hour or more, the mixtures, weighing 50 to 100 grams, were placed in 10-gram or 20-gram fire-clay crucibles and heated in a muffle furnace. The muffle had been heated to the required temperature before the crucibles were placed in it, and thus the crucibles and their contents were heated quickly. When the time allowed for reduction was less than one hour it was rather difficult to get satisfactorily concordant data with this size of charge and method of heating. In order to reduce the heating period to a minimum, these reductions were made with much smaller charges, 5 to 10 grams, and were effected in porcelain crucibles.

In the data following most of the temperatures recorded are the temperatures measured near the crucibles during the period of reduction. Several temperatures, however, were measured in the charge itself, after the charge had come to the temperature of the muffle. In the tests, care was taken to have the heating of the muffle so regulated that the temperature did not vary more than  $15^\circ$  or  $20^\circ \text{ C}$ . either way from that desired. Thus, in the tables following, if the temperature is given as  $700^\circ \text{ C}$ , the temperature was in reality between  $680^\circ$  and  $720^\circ \text{ C}$ ., which was sufficiently close for the purposes of the investigations.

In making these reductions, it was very important as nearly as possible to keep the air from coming into contact with the material. Thus, the crucibles were covered with a clay cover ground to fit the crucibles. In some tests a charcoal cover about 2 mm. (0.04 inch) thick was placed on the charge. Even with the tight covering, in some of the tests there was a slight reversion of the sulphide back to the sulphate, owing possibly to a slight porosity of the crucible walls allowing air to pass through. Some of the data concerning this reversion are given later.

#### TABULATED RESULTS OF TESTS.

In Tables 9 and 10 following are summarized the results of 76 tests made under conditions that were closely similar, so that the results are comparable. In these tests, the carbon added was 20.6 per cent of the weight of the barium sulphate. The barium sulphate used was the precipitated material. The carbon was pulverized to pass a 160-mesh screen, and was mixed with sulphate to the degree that, to the eye, the mixture looked homogeneous.

The variables were the time allowed for reduction and the temperature. Many of the figures given in the tables are the averages of several determinations that in most cases gave concordant results.

TABLE 9.—*Results of reduction tests of barium sulphate showing total barium in reduced product in form of water-soluble barium sulphide.<sup>a</sup>*

Time allowed for reduction.	Per cent of total barium present in reduced product as water-soluble barium sulphide at temperature of—							
	700° C.	750° C.	800° C.	850° C.	900° C.	950° C.	1000° to 1100° C.	1100° to 1200° C.
<i>Minutes.</i>								
15					48		75	96
30	12	29	51	58	65	76	84	97
60	26	35	61	69	85	89	96	
90	28	55	63	78	87	92		
120	41	59	68	85	88	95		
240	65	78	82	86				
360	77							

<sup>a</sup> Tests by W. Freeman, R. Buhman, C. E. Brandt, and V. P. Edwardes.

TABLE 10.—*Results of reduction tests of barium sulphate showing total barium in reduced product in compounds soluble in dilute hydrochloric acid.<sup>a</sup>*

Time allowed for reduction.	Per cent of total barium present in reduced product as compounds soluble in dilute hydrochloric acid at temperature of—							
	700° C.	750° C.	800° C.	850° C.	900° C.	950° C.	1000° to 1100° C.	1050° to 1150° C.
<i>Minutes.</i>								
15					54		80	98
30	21	38	57	65	72	80	89	100
60	37	47	70	78	94	94	100	
90	40	69	75	87	97	97		
120	54	73	85	94	99	100		
240	80	93	98	98				
360	93							

<sup>a</sup> Tests by W. Freeman, R. Buhman, C. E. Brandt, and V. P. Edwardes.

It is to be noted that there is less difference between the percentage of the barium present in acid-soluble compounds and that present as water-soluble barium sulphide in the products of reduction effected at higher temperatures for a short period of time, than in products from reductions at lower temperatures over longer periods.

Most of the products from the 76 reduction tests summarized above contained excess carbon. Other series of tests were made to determine to what extent a decrease in the amount of carbon present in the charge affected the reduction.

When the tests were made with a porcelain crucible fitted with an ordinary porcelain cover, there was frequently sufficient air leaking into the crucible to allow either burning of a small percentage of the carbon, or reoxidization of a small amount of the reduced sulphide

which thus became sulphate. As the data from these tests were, therefore, not entirely accurate, they are not presented here.

Similar reductions were repeated in porcelain crucibles, when a light layer of carbon was placed on top of the charge and other precautions were taken to keep the air from coming into contact with the charge during cooling, etc. Although it was determined that the carbon cover did have some slight reducing action on the charge, yet it was decided that the data obtained were sufficiently accurate for recording in this report, and they are given in Table 4 following.

Later reduction tests, effected in an atmosphere of nitrogen, which was neither oxidizing or reducing, gave results that checked the above data fairly closely.

TABLE 11.—*Results of tests involving reduction of barium sulphate at different temperatures in porcelain crucibles with variable amounts of carbon.<sup>a</sup>*

Temper- ature.	Time.	Parts of carbon per 100 parts of barium sulphate.	Per cent of total Ba in prod- uct, present in—			Per cent of total carbon consumed.	Parts of carbon con- sumed to 100 parts of BaSO <sub>4</sub> , reduced to BaS.
			BaS.	Acid-solu- ble com- pounds.	Insoluble compounds.		
° C.	Minutes.						
800	60	10.5	50	58	42	69	14.5
800	60	21.0	51	56	44	49	20.2
800	120	10.5	62	70	30	83	14.2
800	120	21.0	66	65	32	65	20.5
850	60	10.5	66	70	30	86	13.2
850	60	15.5	60	65	35	65	16.8
850	60	20.5	60	70	30	58	19.8
850	120	10.3	78	85	15	97	12.9
850	120	15.5	76	82	18	84	17.0
850	120	20.6	74	80	20	70	19.4
900	60	10.3	80	85	15	100	12.9
900	60	15.5	81	83	17	87	16.7
900	60	20.6	76	80	20	72	19.4
900	120	10.3	80	86	14	100	12.9
900	120	15.5	84	90	10	89	16.5
900	120	20.6	83	87	13	80	19.8
950	30	10.3	80	83	17	100	12.5
950	30	20.6	84	87	13	78	19.0
950	60	40.0	78	79	21	59	.....
950	60	10.3	94	97	3	100	12.8
950	60	20.6	95	96	4	93	20.2
950	60	30.0	82	82	18	61	23.4
1,050	30	10.3	82	86	14	100	b 11.2
1,050	30	15.5	96	98	2	100	16.1
1,050	30	20.6	95	96	4	89	18.7
1,150	20	10.3	90	90	10	100	11.5
1,150	20	15.5	99	99	1	100	15.6
1,150	20	20.6	99	100	0	90	18.2

<sup>a</sup> Tests by W. Freeman, R. Buhman, C. E. Brandt, and V. P. Edwardes.

<sup>b</sup> This factor may be slightly low, owing to a slight reducing action of the carbon cover.

In another set of reduction tests the barium sulphate was mixed intimately with finely pulverized carbon and placed in a porcelain tube in an electrically heated tube furnace. The tube was filled with nitrogen gas at the start, and the gases evolved were discharged through a water seal or into caustic-potash solutions. Thus neither oxygen nor any reducing gases other than the carbon monoxide from

the carbon came in contact with the barium sulphate. The results are given in Table 12 following:

TABLE 12.—*Results of tests involving reduction of barium sulphide by carbon in tube furnace, surrounded by atmosphere of nitrogen.<sup>a</sup>*

Temperature. ° C.	Parts of carbon per 100 parts of $\text{BaSO}_4$ in charge.	Per cent of total carbon consumed.	Per cent of $\text{BaSO}_4$ reduced to $\text{BaS}$ .	Carbon con- sumed per 100 parts of $\text{BaSO}_4$ reduced.
800	10	80	58	13.8
800	10	100	70	14.3
800	20	63	64	19.8
900	10	95	70	13.5
900	10	100	74	13.5
950	10	97	75	12.9
950	10	100	75	13.3
950	15	90	82	16.4
950	14	100	96	14.7
950	15	100	90	16.7
1,000	10	100	80	12.5
1,000	15	100	96	15.6
1,000	20	84	95	17.6

<sup>a</sup> Tests by W. Freeman and V. P. Edwardes.

#### COMMENTS ON RESULTS OF TESTS.

The tabulated data indicate that the carbon efficiency was greatest when the charge contained the smallest percentage of carbon. In general, somewhat higher carbon efficiency was obtained in the reductions effected at the higher temperatures than at the lower.

Although the highest carbon efficiency (about 12 to 12.5 per cent) was obtained when the carbon present was about 10 per cent of the barium sulphate, the theoretical amount if the carbon was oxidized completely to carbon dioxide, yet with this amount of carbon the maximum reduction of the barium sulphate at temperatures up to 1,000° C. was only about 80 per cent. With 15 per cent carbon present in the charge, the reduction was nearly complete when the carbon was consumed.

When the carbon was present to the extent of 20 per cent of the  $\text{BaSO}_4$ , the carbon efficiency was much lower irrespective of whether the reduction was at high or low temperatures, but slightly higher at the high temperatures than at the low.

From these data it is to be noted, also, that with an excess of carbon the reduction seemed to proceed slightly slower than did the reduction with the lesser amount of carbon present. This is shown especially in the results of series at 850°, 900°, and 950° C., shown in Table 4.

However, it must be recognized that the fineness to which the material is pulverized, and the intimacy with which the sulphate and carbon are mixed, are factors influencing these results, as is the depth of material through which the carbon monoxide gas must pass

before leaving the charge. For example, in several tests "straight" barium sulphate was placed on top of the charge containing 20 per cent carbon. This barium sulphate cover was largely reduced by the carbon monoxide coming up from the charge proper, thus increasing the efficiency of the carbon when credited with the whole amount of barium reduced.

Summarized briefly, the data from the Series 2 tests show that when the carbon and the barium sulphate were finely pulverized and intimately mixed, and the reduction was effected in a muffle or crucible type of furnace, in the absence of outside air or of products of combustion of fuel, and at temperatures between 850° and 1,000° C., a high reduction (90 per cent or better) could be obtained when the carbon added was about 15 per cent of the barium sulphate. With the addition of less carbon, although the carbon efficiency was greater, the reduction was not so complete. With the use of more than 15 per cent carbon, the carbon efficiency decreased, unless provision was made to utilize the carbon monoxide issuing from the charge by passing it through another charge of barium sulphate.

Different kinds of barium sulphate gave different results in the reductions carried on under the same conditions. For example, the following materials, all finer than 200-mesh, were reduced at the same time under the same conditions, that is, a temperature of 900° C. and a reduction period of 120 minutes, with the following results:

*Results of reduction tests of different kinds of barium sulphate.*

Material.	Per cent of total barium in product in —		
	Water-sol- uble com- pounds.	Water- insoluble, acid-solu- ble com- pounds.	Acid- insoluble com- pounds.
Precipitated BaSO <sub>4</sub> , 99.6+ per cent.....	88	10	2
Pulverized barytes, 98 per cent BaS <sub>4</sub> .....	78	13	9
Pulverized barytes, 92.5 per cent BaSO <sub>4</sub> .....	72	18	10
Precipitated BaSO <sub>3</sub> +BaSO <sub>4</sub> .....	93	7	0

In the pulverized barytes containing 98 per cent barium sulphate the impurities were barium carbonate, iron, and silica. In the barytes containing only 92.5 per cent barium sulphate there was about 3 per cent iron and 3 per cent silica.

Some comparative tests were made to determine the effect of iron on the reduction of barium sulphate. Four charges were made up in which iron to the extent of about 6 per cent was mixed with the precipitated barium sulphate. In one charge the iron was added as ferric sulphate, in another as ferrous ammonium sulphate, in a third

as ferrous sulphate, and in a fourth as ferric oxide. Two charges of the pure precipitated barium sulphate were reduced under the same conditions—a temperature of 850° C. and a reduction period of 120 minutes. The average results of four tests were as follows:

*Results of reduction tests in which iron was added to reduction charge.*

Material reduced.	Percent of total barium present in—		
	Water-soluble compounds.	Water-insoluble, acid-soluble compounds.	Insoluble compounds.
Pure BaSO <sub>4</sub> .	80	10	10
BaSO <sub>4</sub> with 6 per cent of iron present	68	17	15

#### REOXIDATION OF BARIUM SULPHIDE TO SULPHATE.

It has been stated that barium sulphide, when at red heat, is readily reoxidized to the sulphate. The data from several of the crucible-reduction tests were found to be of no value because inadequate precautions were taken to prevent the oxygen from getting into the crucible. An example of the effect of small air leakages into the crucible is given below. These results were obtained when pulverized barytes (98 per cent BaSO<sub>4</sub>) was reduced with 20 per cent willow charcoal at 1,000° C.

*Results of reduction tests in which air leaked into reduction crucible.*

Time of reduction.	Per cent of barium in product present in			Condition of cover.
	Water-soluble BaS.	Water-insoluble, acid-soluble compounds.	Insoluble BaSO <sub>4</sub> .	
<i>Minutes.</i>				
60	94	6	—	Tight.
60	76	3	21	Loose.
120	56	4	40	Loose.
120	35	3	62	Very loose.

The reoxidation product is the sulphate, not the oxide. This fact is shown in the results presented in the foregoing table, also in the results of some special tests that were made to determine the product of oxidation of barium sulphide. In these tests material containing 95 per cent of the barium as the sulphide was heated in the air for varying periods of time at different temperatures. In most cases practically all the sulphide was reconverted to the sulphate, and only small amounts of oxide were formed. The maximum

conversion to oxide was about 7 per cent, and was obtained when the material was heated to 800° C. for two hours.

#### SERIES 3 TESTS.

In the Series 3 tests, barium sulphate mixed with carbon and made into briquets was reduced in a shaft furnace heated by oil. Precipitated barium sulphate was mixed with lampblack carbon from the local gas works, and the mixture was pressed into the form of cupels, 2.5 cm. (1 inch) in diameter and 3.2 cm. ( $1\frac{1}{4}$  inches) high. These cupels were dried and then were charged into a small shaft furnace 30.5 cm. (12 inches) in diameter, and 76.2 cm. (30 inches) high. This furnace was heated to about 950° to 1100° C. by oil, the products of combustion passing through the shaft and maintaining strongly reducing conditions around the briquets. The furnace was kept filled with briquets during a test, more briquets being added at the top as the reduced product was withdrawn below. The length of time the briquets were in the furnace varied between one and one-half and three hours. During an average run of six hours there was about 80 kilograms (176 pounds) of the briquets reduced. The best average product obtained from any of the runs contained 82.5 per cent of the barium as sulphide, 13.8 per cent as oxide and carbonate, and 3.7 per cent as insoluble sulphate. The best product from any charge during this run contained 87 per cent of the barium as sulphide. During this run the maximum furnace temperature was 1150° C. The average carbon monoxide content of the gases in the shaft of the furnace was 4 per cent.

In this shaft furnace several runs also were made with briquets of pulverized commercial barytes (92.5 per cent BaSO<sub>4</sub>) and lampblack carbon. These briquets were 6.36 cm. (2½ inches) long, 6.35 cm. (2½ inches) in diameter, and weighed each about 370 grams (or 0.81 pound). With these briquets unsatisfactory reductions were obtained, even though the temperature of the furnace was raised to 1100° C., and broken pieces of coke were charged with the briquets. The best products contained only about 70 per cent of the barium as sulphide. Also, unless the large briquets were broken and chilled immediately on being removed from the furnace, they retain their heat for a long time, and the barium sulphide to a great extent oxidized back to the sulphate.

One charge of reduced briquets weighing about 25 kilograms, and containing at the time of withdrawal from the furnace about 70 per cent of the barium as sulphide, was allowed to stand unbroken in an iron container for about 15 hours. At the end of this time, the briquets in the center of the container were still glowing. The

outside cooled briquets contained less than 15 per cent of the barium as sulphide, the rest having oxidized back to sulphate.

#### SERIES 4 TESTS.

In the Series 4 tests barium sulphate was reduced in a multiple-hearth furnace.

##### DESCRIPTION OF MULTIPLE-HEARTH REDUCTION FURNACE.

The furnace (Pl. I, *B*, and Pl. II, *A*) was designed by Mr. Utley Wedge, and was loaned to the bureau's representatives for the investigations.

The furnace was 24 inches (61 centimeters) in inside diameter and 34 inches (86.3 centimeters) high; that is, between the bottom of the cast-iron drying hearth 7 (Pl. I, *B*) to the top of the bottom hearth 12. Beneath the bottom hearth was a calcine pit 12 inches deep. Above the drying hearth were placed the driving gears, roller bearings, etc. The total height over all was 6 feet (1.83 meters).

The walls of the furnace were of specially molded fire brick 8 inches (20.3 centimeters) thick, containing openings for gas burners, pyrometer tubes, gas-sampling tubes, and mica windows, or peepholes. Outside the brick walls of the furnace was placed a covering of magnesia board 1½ inches thick. This magnesia was covered with a layer of asbestos cement one-eighth inch thick, over which was placed a thin layer of Portland cement.

In the center of the furnace was hung a cast-iron column, 1 (Pl. I, *B*), 3½ inches (95.2 centimeters) in diameter, which was keyed into the center of a gear wheel, 36 inches (0.915 meter) in diameter, revolving on roller bearings, 3. These roller bearings were carried on a horizontal cast-iron bedplate, 4, resting on four short adjustable pins, 5. The pins were screwed into sockets in the flange 6 of the drying plate 7. This drying plate was bolted to four steel columns, 8, placed outside the walls of the furnace. The upper bearing for the center column was carried on a steel frame, 9, which was also bolted to the four steel columns. The large gear, meshed with a worm drive, 10, was bolted to the bedplate 4. At one end of this worm-drive shaft was placed a pulley, 11, over which belt connection was made to a driving motor.

To the revolving center column inside the furnace were attached three cast-iron hearths (13, II, *A*; see also figs. 2 and 3) 22 inches (55.9 centimeters) in diameter. Thus, there was an annular space 1 inch (2.54 centimeters) wide between these hearths and the furnace walls. Between these movable hearths and below the lowest were placed three stationary hearths 12 (Pl. II, *A*), resting on shelves

provided on the brick walls. The opening at the center of these hearths was 6 inches (15.25 centimeters) in diameter, leaving an annular space 1 inch wide between the stationary hearths and the

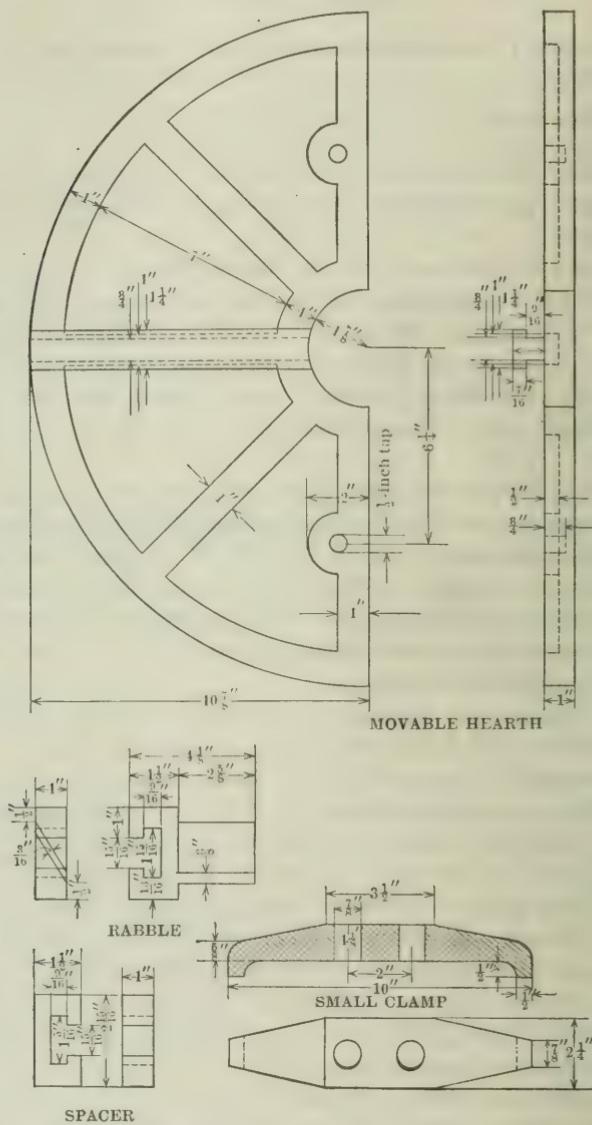
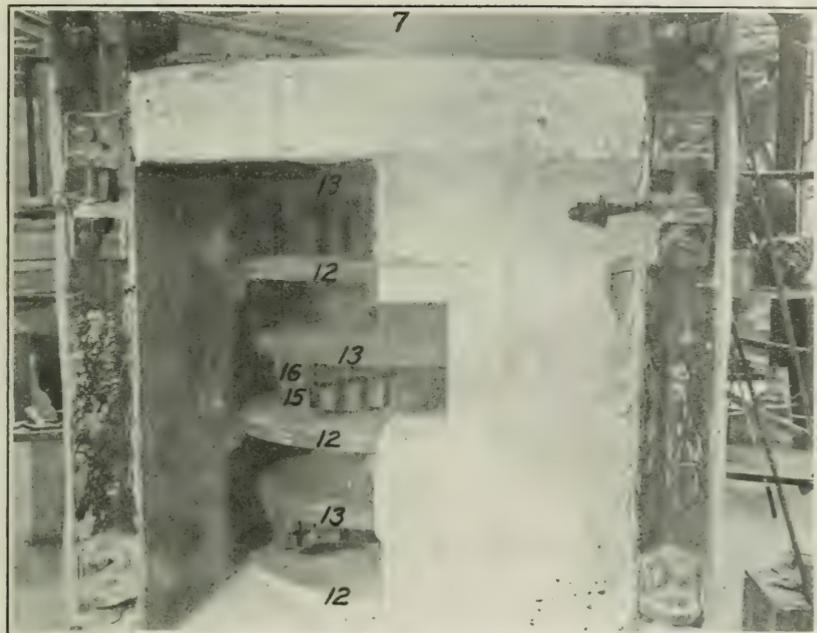


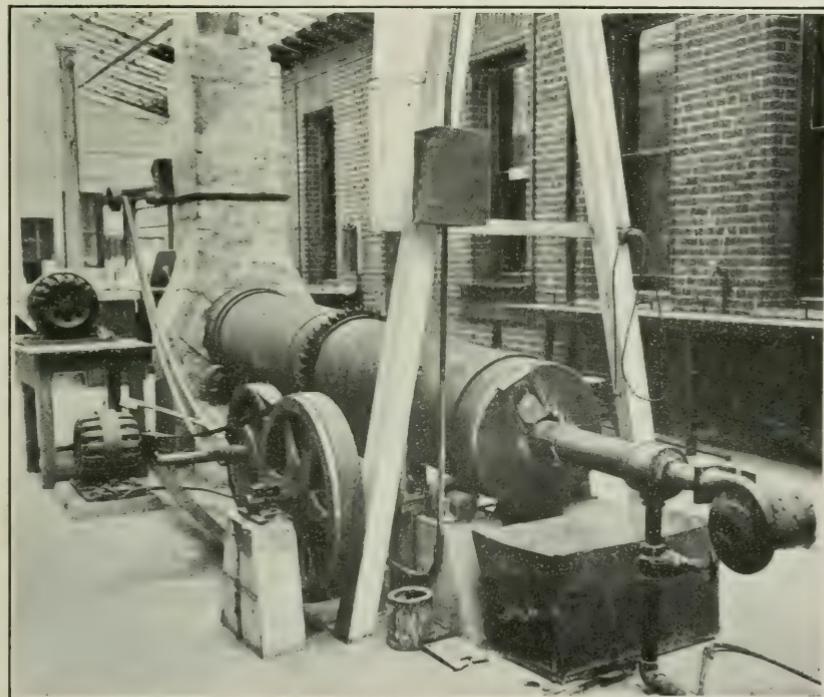
FIGURE 2.—Details of a movable hearth in multiple-hearth furnace.

center columns. The total effective hearth area was 16.5 square feet (1.53 square meters).

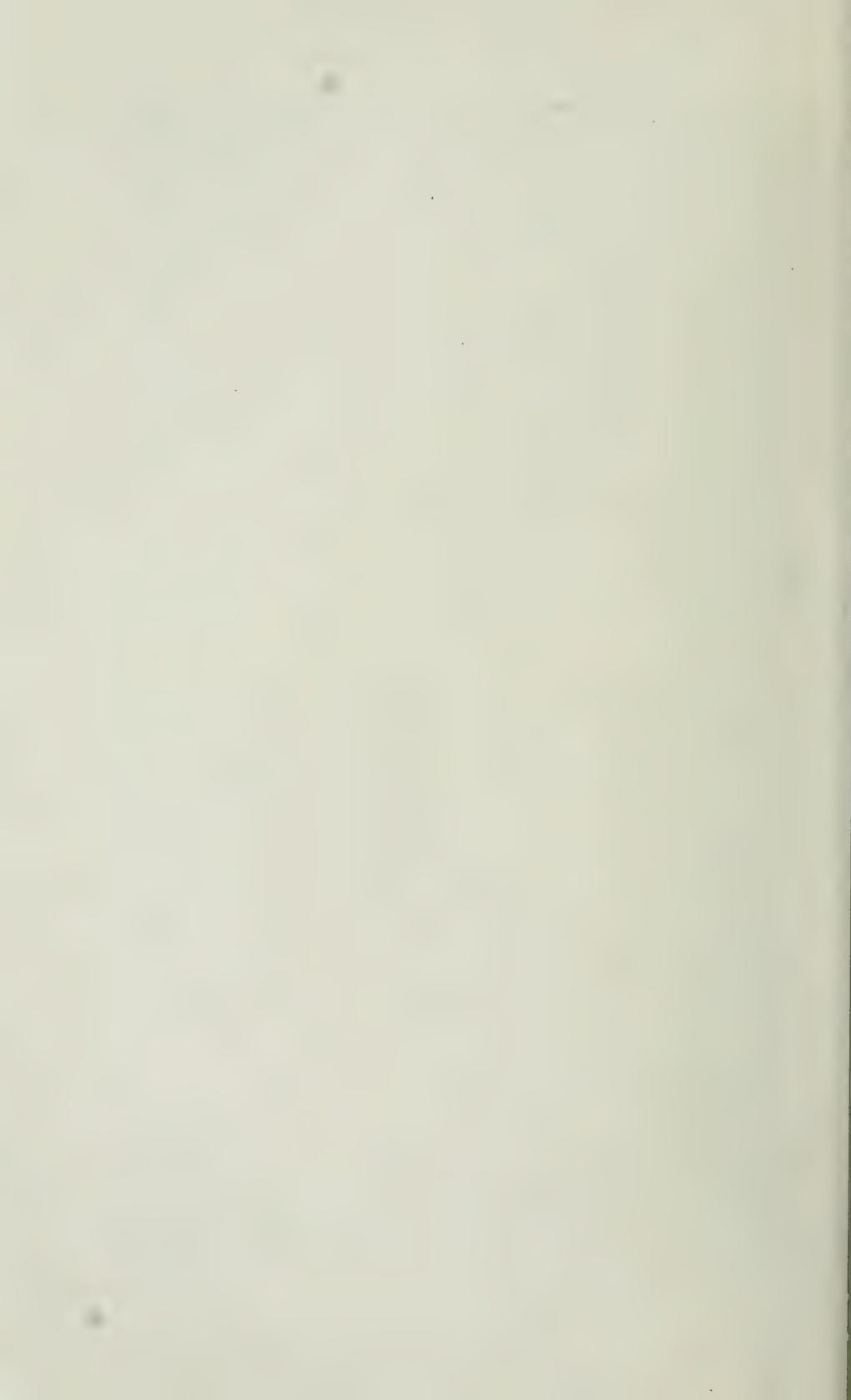
Rabbles (15, Pl. II, A; see also figs. 2 and 3) were attached to ribs (16, Pl. II, A) cast on the underside of the hearths. The rabbles



A. INTERIOR OF FURNACE, SHOWING CAST-IRON HEARTHS AND RABBLES.



B. CEMENT KILN USED IN REDUCTION TESTS AT HIGH TEMPERATURES.



stirred and moved the ore across the hearths immediately below. The ore on the cast-iron drying floor (7, Pl. I, B) was moved by the rabbles (17, Pl. I, B) revolving with the center column. From the drying floor the ore fell to the center of the top movable hearth and was moved by the rabbles suspended from the stationary drying

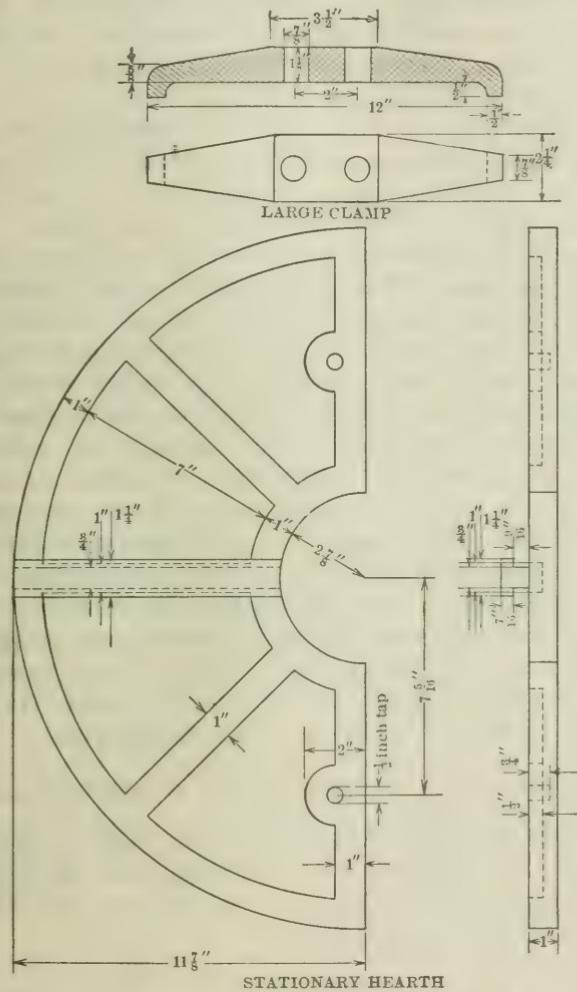


FIGURE 3.—Details of a stationary hearth in multiple-hearth furnace.

hearth to the outside of the top revolving hearth, falling onto the second hearth, a stationary hearth. It was then moved by rabbles attached to the top movable hearth to the center of the stationary hearth and fell onto the third hearth, a moving hearth. The ore was thus moved through the furnace in a manner similar to that in a regular large-size multiple-hearth roasting furnace.

The cast-iron hearths lasted for many tests when the temperatures were not over 800° C., but when temperatures above 900° C. were maintained they warped and cracked and had to be replaced after eight or nine 12-hour runs.

Bristol pyrometers (18, Pl. I, B) were inserted through the walls of the furnace for measuring the temperature on the first, third, and fifth hearths. Gas samples were also drawn from the furnace at these hearth levels. Peepholes (19, Pl. I, B) were provided at several points for observing the charge in the furnace.

Movable brick plugs (20, Pl. I, B) were provided in the walls of the furnace, which gave access to the interior for cleaning off the hearths. The movable plugs were somewhat necessary, as some charges had a tendency to ball up in front of the rabbles.

The furnace was heated by oil fuel or by city gas. In most of the tests gas was used. The gas was burned through Meker burners (21, Pl. I, B), with a 20-pound air pressure at the burners.

It is not considered that the fuel consumption in this furnace furnished data for calculating the fuel that would be required in a standard furnace of this type if properly designed to prevent radiation losses, etc. The center revolving column was water cooled. The cooling water removed one-fifth to one-third of the total heat supplied to the furnace by the combustion of the gas. In most of the reduction tests the furnace was operated under only a slight draft—just enough to allow the products of combustion, etc., to be removed from the furnace through the flue (22, Pl. I, B).

In straight roasting, when pyrites containing 35 to 40 per cent sulphur were being roasted, the furnace, once heated, could be run several hours, roasting at the rate of 30 or 35 pounds (13.6 to 16.1 kilograms) per hour without the use of extraneous fuel.

#### SUMMARY OF REDUCTION TESTS IN FURNACE.

Following are summarized briefly 20 tests made in the furnace. In making the reduction tests the variables were as follows: (1) Length of time the material was in the furnace; (2) the furnace temperature; (3) reducing conditions.

#### REDUCTION PERIOD.

The length of time the material was in the furnace was controlled by the rate at which the charge was fed and by the speed of revolution of the center column. The rate of feeding was varied between 5.6 to 19.8 pounds ( $2\frac{1}{2}$  to 9 kilograms) per hour, and the length of time the material was in the furnace varied between 2 and  $3\frac{1}{2}$  hours.

## FURNACE TEMPERATURES.

The variations in the furnace temperatures were as follows:

*Furnace temperatures in reduction tests.*

Part of furnace.	Minimum temperature.	Maximum temperature.	Average temperature.
First hearth.....	° C. 180	° C. 485	° C. 360
Third hearth.....	560	905	800
Fifth hearth.....	840	920	850

## REDUCING CONDITIONS.

In all tests the quantity of city gas used was in excess of that required for the combustion to maintain the proper temperatures. In the 20 tests summarized, no free oxygen was allowed in the furnace. The carbon monoxide content of the gases taken from the furnace on the third and fifth hearth ranged between 0.5 and 5 per cent. The fuel-gas consumption was between 3 and 6 cubic feet per minute. The main consideration in these tests was to obtain the maximum reduction rather than the highest efficiency of the reducing agent—carbon or gas.

These 20 reduction tests may be divided into the following groups:

1. Tests involving reduction of precipitated barium sulphate (99 per cent  $\text{BaSO}_4$ ) intimately mixed with lampblack carbon, heavy oil residuum, pulverized coke, or powdered charcoal.
2. Tests involving reduction of precipitated barium sulphate (99 per cent  $\text{BaSO}_4$ ) with excess hydrogen, carbon monoxide, or hydrocarbons entering the furnace through the burners, no carbon being mixed with the material.
3. Tests involving reduction of commercial pulverized barytes (98 per cent  $\text{BaSO}_4$ , as used in paints by the W. P. Fuller Co.) with coke, lampblack, carbon, or like material mixed intimately with the barytes.

## TABULATED RESULTS OF TESTS.

The results of the tests are given in Table 13 following:

TABLE 13.—*Results of reduction tests in multiple-hearth furnace.*

[Tests by A. E. Wells, A. L. Tuttle, W. Freeman, R. Buhman, and C. E. Brandt.]

REDUCTION OF PRECIPITATED BARIUM SULPHATE (99.4 PER CENT BASO<sub>4</sub>) INTIMATELY MIXED WITH LAMPBLACK CARBON, HEAVY-OIL RESIDUE, POWDERED CHARCOAL, POWDERED COKE OR FLUORERIZED COKE.

Test No.	Parts of carbon per 100 parts of BaSO <sub>4</sub> in charge.	Character of carbon used.	Rate of charging mixture per hour.	Approximate length of time material was in furnace.	Average temperature.		Maximum temperature in furnace.	Average per cent of CO in furnace gases (third hearth).	Analysis of product of test. <sup>a</sup>			
					Total time of test.	Top hearth.	Third hearth.	Writhe hearth.	Total Ba water soluble.	Total Ba acid soluble.	Total Ba insoluble BaSO <sub>4</sub> .	Per cent.
1	20	Lampblack.....	8.9	5.2	Hours.	Hours.	°C.	°C.	°C.	Per cent.	Per cent.	Per cent.
2	16	do.....	5.0	2 <sup>1</sup> / <sub>2</sub>	8	180	560	810	840	4.5	35	65
3	20	Pulverized coke.....	3.5	3.0	2 <sup>1</sup> / <sub>2</sub>	9	270	590	860	5.0	71	12
4	25	do.....	3.5	3.7	12	300	640	880	990	4.7	75	93
5	25	Pulverized coke.....	3.5	4.6	3	270	570	890	935	1.6	55	78
6	17	do.....	3.0	3.5	9	420	760	895	905	2.0	77	92
7	18	do.....	3.0	3.5	3 <sup>1</sup> / <sub>2</sub>	10	370	810	890	905	5	80
8	15	do.....	3.5	4.5	3 <sup>1</sup> / <sub>2</sub>	10	370	790	885	910	5	82
					12	460	890	900	900	2.0	77	90

REDUCTION OF PRECIPITATED BARIUM SULPHATE (99+ PER CENT BaSO<sub>4</sub>) BY EXCESS H<sub>2</sub>, CO, OR HYDROCARBONS ENTERING FURNACE THROUGH BURNERS. NO CARBON MIXED WITH MATERIAL.

REDUCTION OF PULVERIZED COMMERCIAL BARYTES (AS USED IN PAINTS BY W. P. FULLER CO.), WITH COKE, LAMPBLACK CARBON, ETC., MIXED INTIMATELY WITH BARYTES, ETC.

C-1	20	Pulverized coke.....	3.5	3.8	2.8	12.2	760	870	910	0.5	51	59	41	60
C-2	20	...do.....	3.2	4.5	2.4	8	410	895	900	1.0	65	75	25	68
C-3	20	Lamphblack.....	3.5	5.0	3	6	380	760	890	2.5	68	80	20	72
C-4	20	Pulverized coke.....	3.0	4.2	3	7	410	780	865	1.0	68	80	20	72
D-1	0.0	.....	3.0	5.0	.....	10	490	850	890	1.0	68	80	20	72
D-2	0.0	.....	3.0	5.4	.....	11	410	820	880	2.0	64	75	25	72
D-3	0.0	.....	3.0	5.5	.....	10	420	810	900	4.2	68	82	18	72

a Note maximum reduction

Note that  $\sin \alpha$  is reduced.

In tests designed by a figure given by the letter D, no carbon was used, reduction being effected by gases alone.

## COMMENTS ON RESULTS OF TESTS.

The results presented in Table 13 indicate that with precipitated barium sulphate the highest reductions were obtained when the material was mixed with carbon either as pulverized charcoal or lampblack, and when the higher temperatures were maintained in the furnace. Under these conditions the percentage of excess reducing gases present in the furnace could be decreased to a low figure.

The pulverized commercial barytes were more difficult to reduce than was the precipitated barium sulphate.

When the maximum temperature in the furnace was above 850°C., the material was slightly sintered into balls about 0.3 centimeter (1.8 inches) in diameter, like cement cinders. The slightly sintered balls formed in the first reductions were somewhat broken and the material was pulverized readily for subsequent use as a precipitant in the solutions.

It is to be regretted that reduction tests at higher temperatures—above 900°C.—could not have been made with this type of furnace. However, refractory hearths to withstand higher temperatures over longer periods of time were not available.

## SERIES 5 TESTS.

In the Series 5 tests barium sulphate was reduced in a cement kiln.

Through the courtesy of the chemistry department of the University of California, a small cement kiln (Pl. II, B) was made available for further work on the reduction of barium sulphate at high temperatures.

This cement kiln was 3.66 meters (12 feet) long, 48.3 centimeters (19 inches) in outside diameter, and 25.4 centimeters (10 inches) in inside diameter. The number of revolutions was 1.15 per minute, and the pitch was 1:18.

In the tests with this furnace, city gas or oil fuel was used for heating. The lower end of the kiln was closed by a sheet-iron plate covered with asbestos. Through this plate a gas burner was inserted, the gas being blown in with air under low pressure. A small gate was provided in this sheet-iron plate to allow drawing out the reduced product intermittently.

The gaseous products of the kiln were discharged into a brick stack. The draft at the furnace was reduced to a minimum, so that the reducing conditions in the furnace could be controlled by the air and gas entering through the burner pipe. Even with the draft reduced to a minimum, there was considerable barium sulphate carried out of the furnace by the gases. In one test when oil was used and was being discharged through the burner by a high air pressure, directly along the center line of the kiln, the loss of barium sulphate was high—about 30 per cent. When this oil-and-air mixture was discharged at right angles with the center line, striking against the sides of the kiln, the loss was greatly reduced, but was not less than 5 per cent under any conditions.

Provision was made for taking samples of gas at several points along the length of the kiln, and also for measuring the temperatures at these points by thermocouples.

The charge to the furnace was fed in by hand at the back of the furnace.

In these reduction tests, the temperature at the hottest part of the furnace was as high as 1,100° C., and averaged 1,050° C. For over half of the furnace the temperature was above 850° C. The average time the charge was in the furnace was 2½ hours. The average rate of feeding the charge to the furnace was 15 kilograms (33 pounds) per hour, ranging between 10 and 20 kilograms per hour. The best reductions were obtained when the furnace was kept well filled with the charge.

In these tests, the material used was finely pulverized barytes (98+ per cent BaSO<sub>4</sub>), being material used in paints by the W. P. Fuller Co., as large quantities of the precipitated barium sulphate could not be obtained. In six tests city gas was used, and in one test oil was used for fuel. The main object in the tests was to obtain a high reduction of the barium to the water-soluble sulphide, the obtaining of a higher efficiency of the reducing agent being a secondary consideration. However, one test (5-7), was conducted for the purpose of obtaining a higher fuel efficiency than was obtained in the other tests. This test showed that almost as high a reduction could be obtained with a much less fuel consumption.

None of these tests furnished conclusive data for calculating the amount of fuel that would be required for effective reduction in a commercial sized kiln.

The results of the tests with the cement kiln are given in Table 14 following:

TABLE 14.—Results of tests involving reduction of commercial pulverized barytes in cement kiln.

[Tests by A. E. Wells, W. Freeman, R. Buhman, and V. P. Edwardes.]

Test No.	Parts carbon per 100 parts BaSO <sub>4</sub> in charge.	Character of carbon used.	Rate of charging mixture per hour.	Rate of gas consumption per minute.	Average temperature of exit gases.	Average temperature at middle of kiln.	Approximate maximum temperature in kiln.	Average percent of CO in furnace gases at middle of furnace.	Total time of test.	Analysis of product of test.		
										P. ct.	P. ct.	Total Ba-wa-ter soluble.
5-1	20	Pulverized coke.....	Kilos.	Cu. ft.	°C.	°C.			Hours.	P. ct.	P. ct.	P. ct.
5-2	15	.....do.....	10.0	5.4	450	850	1,050	3.8	22½	89	98	2
5-3	20	Pulverized charcoal.....	10.0	5.6	460	880	1,050	4.2	10	87	97	3
5-4	16	.....do.....	15.0	6.1	420	880	1,100	3.1	5	90	98	2
5-5	.....do.....	15.2	6.3	400	860	1,050	4.2	5	89	98	2	
5-6	18	Pulverized coke.....	15.5	6.2	510	900	1,100+	6.2	4	a 69	78	22
5-7	13	Coke.....	16.0	(3)	.....	1,360	(c)	2	2	84	96	4
			18.7	3.8	370	840	1,050	1.5	4	82	90	10

<sup>a</sup> Product clinkered and unreduced BaSO<sub>4</sub> was left in the interior of the clinker.

<sup>b</sup> Rate of oil consumption, 3 gallons per hour.

<sup>c</sup> No data.

**SUMMARY OF DATA CONCERNING REDUCTION OF BARIUM SULPHATE IN FIVE SERIES OF TESTS.**

Summarizing briefly the data obtained in the five series of reduction tests outlined above, it may be stated that the maximum reduction of the barium sulphate to sulphide was obtained at the higher temperatures—that is, around 1000° C., and when the reductions were effected in an indirect-fired furnace, as, for example, a muffle furnace. When reductions were effected in this type of furnace, 15 or 16 per cent carbon gave the highest fuel efficiency consistent with the completeness of the reduction of the barium to the sulphide.

In reductions effected in a direct-fired furnace, as a cement kiln, a multiple-hearth roasting furnace or a shaft furnace in which hydrogen, hydrocarbons, or the products of combustion of the fuel—water and carbon dioxide—were brought into contact with the sulphate or sulphide, there was formed a larger proportion of barium compounds, insoluble in water, than was formed in a furnace indirectly fired. Thus, although the barium compounds in the best products from a direct-fired furnace were 90 to 95 per cent soluble in acid, yet the barium present as the water-soluble sulphide was not more than 85 to 87 per cent of the total.

By effecting the reductions rapidly at high temperatures—that is, above 1000° C.—the proportion of these water-insoluble barium oxides and carbonates was less than that formed in reductions at lower temperatures over a longer period of time.

Below 750° C. the reduction by carbon or reducing gases was too slow to be considered commercially feasible.

From these data it is concluded that in order to effect the maximum reduction of the sulphate to the water-soluble sulphide the reductions should take place in an indirect-fired furnace at high temperatures. This means a muffle-type furnace or a furnace built along the lines of a modern coal-gas producer.

**TESTS TO DETERMINE DECREASE OF BARIUM SULPHIDE IN REDUCED PRODUCTS FROM CYCLIC OPERATIONS.**

As stated in the above discussion concerning reduction, in none of the reductions effected in the shaft furnace, the multiple-hearth furnace, or the cement kiln where these reducing gases or water vapor came in contact with the material did the final reduced product contain less than 8 per cent of the barium as a water-insoluble product, which was principally the oxide.

In the regular precipitations of the cyclic operations, these slowly soluble or insoluble barium compounds reacted rather slowly with the sulphur dioxide in the dilute solutions left after the greater part of the sulphur dioxide had reacted with the readily soluble sulphide.

Thus in the cycles a large proportion of these compounds was not converted into the sulphite or sulphate in the precipitation operation, but was carried around in the cycles as "inactive" material. As in each reduction stage there was a certain amount of these "inactive" compounds formed, the proportion of these gradually increased to such a point that, in several cyclic tests, more than half of the material used was of little or no service as a precipitant.

Summaries of these data from three cyclic tests are given in Tables 15, 16, and 17, following:

**CYCLIC OPERATIONS IN WHICH REDUCTIONS WERE MADE IN THE MULTIPLE-HEARTH FURNACE.**

In Table 15 are presented results showing the decrease in the proportion of barium sulphide with a corresponding increase in the proportion of the oxide and carbonate in the products of reduction during four cycles in reduction tests effected in the multiple-hearth furnace.

TABLE 15.—*Results of cyclic operations in which reductions were made in multiple-hearth furnace.<sup>a</sup>*

Material reduced.	Per cent of total Ba present as—				Reduced product No.
	BaS readily soluble in H <sub>2</sub> O.	BaO readily soluble in H <sub>2</sub> O.	BaO, BaS, BaCO <sub>3</sub> , etc., insoluble in H <sub>2</sub> O, soluble in HCl.	Insoluble BaSO <sub>4</sub> .	
Pure BaSO <sub>4</sub> .....	74	2	12	12	1
Precipitate formed by adding reduced product 1 to SO <sub>2</sub> solution.....	70	5	18	7	2
Precipitate formed by adding reduced product 2 to SO <sub>2</sub> solution.....	66	6	24	4	3
Precipitate formed by adding reduced product 3 to SO <sub>2</sub> solution.....	57	8	32	3	4

<sup>a</sup> Tests by A. E. Wells, A. L. Tuttle, W. Freeman, R. Buhman, and C. E. Brandt.

**CYCLE OPERATIONS IN WHICH REDUCTIONS WERE MADE IN CEMENT KILN.**

In Table 16 are given summarized data concerning the products obtained during the operation of the process through six complete cycles, the apparatus shown in Plate I, *A*, being used for absorption, precipitation, decantation, filtration, and drying. The distillations were made in an iron kettle, and reductions were effected in the cement kiln shown in Plate II, *B*.

The reduced product used as a precipitant in the first cycle contained 84.1 per cent of the total barium as sulphide, 5.1 per cent as water-soluble oxide, 8.7 per cent in water-insoluble but acid-soluble compounds, and 2.1 per cent as sulphate. The ratio of sulphur to barium in this material was 0.88 atom of sulphur to 1 atom of barium.

In the precipitate of the first cycle, after distillation, the ratio of sulphur to barium was 0.96 to 1, showing that all the water-soluble oxide, and some of the insoluble compounds had reacted with the sulphur dioxide. In the following reduction stage about 16 per cent of the sulphur in these compounds was lost, so that the reduced product contained a ratio of only 0.80 atom of sulphur per atom of barium.

In the reduction stage of the second cycle, the loss of sulphur from the barium compounds was very high—about 25 per cent—for reasons that were not apparent. The records of that reduction indicate that the same high temperature and strongly reducing conditions prevailed as in other reductions. However, this material was put through the furnace at a much slower rate than in other tests, which meant that a larger proportion of the material was exposed to the gases and the products of combustion than in other reductions.

In the precipitations of the fifth and sixth cycles the sulphur dioxide solutions were not so completely neutralized; that is, more sulphur dioxide was allowed to return to the absorption tower than in the first four cycles. Thus, during the period of precipitation, the insoluble compounds in the reduced material added were in contact with a slightly stronger sulphur dioxide solution after the readily soluble compounds had reacted. The result was that there was a slightly greater proportion of these compounds reacting. Thus, the ratio of sulphur to barium increased in the precipitate and also in the reduced product. The final reduced product after the sixth cycle contained as much barium sulphide as did the reduced product after the second cycle.

TABLE 16.—*Results of reduction tests with cement kiln, involving six cycles.<sup>a</sup>*

Item.	Cycle No.					
	1	2	3	4	5	6
Sulphur dioxide precipitated:						
Volume of solution, liters.....	5,460	3,080	2,850	1,260	1,260	770
Average SO <sub>2</sub> in solution per liter, grams.....	8.75	12.0	9.4	10.45	8.5	8.05
Total SO <sub>2</sub> in solution, kilograms.....	47.7	37.0	26.8	13.2	10.7	6.2
Average SO <sub>2</sub> per liter in solution after precipitation, grams.....	.20	.15	.28	.20	.42	.50
Total SO <sub>2</sub> in solution after precipitation, kilograms.....	1.1	.5	.8	.25	.5	.4
Total SO <sub>2</sub> precipitated, kilograms.....	46.6	36.5	26.0	13.0	10.2	5.8
Per cent of total SO <sub>2</sub> precipitated.....	98.0	98.0	97.0	98.0	95.0	94.0
Reduced material added, kilograms.....	100.0	85.0	80.0	46.0	42.0	25.0
Weight of BaS added, kilograms.....	75.1	56.6	34.6	18.3	13.0	8.2
Water-soluble BaO added, kilograms.....	5.16	4.2	7.0	1.9	1.2	.8
Total theoretical equivalent <sup>b</sup> of reduced material in terms of SO <sub>2</sub> , kilograms.....	44.8	34.0	22.7	11.2	7.8	5.0
Actual SO <sub>2</sub> equivalent of reduced material, per cent of theoretical.....	104.0	107.0	115.0	116.0	129.0	116.0
Ba content of mother liquor after precipitation, grams per liter.....	8.5	6.8	9.2	6.2	10.2	9.5

TABLE 16.—*Results of reduction tests with cement kiln, involving six cycles—Continued.*

Item.	Cycle No.					
	1	2	3	4	5	6
<b>Precipitate:</b>						
Weight of dried precipitate, kilograms.....	135.0	115.0	102.0	57.0	50.5	430.0
Ba in precipitate, per cent of product.....	48.0	53.5	54.2	51.0	49.0	48.5
Per cent of total Ba accounted for in precipitate.....	92.0	101.0	96.0	97.0	95.0	96.0
Per cent of total barium in precipitate present as—						
BaS <sub>2</sub> O <sub>3</sub> .....	86.5	70.6	53.2	48.0	42.0	45.0
BaSO <sub>3</sub> .....	6.5	6.8	13.0	18.0	25.0	25.0
BaO, BaCO <sub>3</sub> +BaSO <sub>4</sub> .....	7.0	22.6	33.8	34.0	33.0	30.0
<b>Distilled precipitate:</b>						
Weight of residual product from distillation.....	117.0	95.0	92.0	51.0	43.0	26.0
Ba in distilled precipitate, per cent of product.....	55.5	65.0	60.0	58.0	56.0	58.0
Per cent of total Bain product present as—						
BaS <sub>2</sub> O <sub>3</sub> .....	0.0	0.0	0.0	0.0	0.0	0.0
BaSO <sub>3</sub> .....	65.6	42.1	29.2	32.5	34.0	35.2
BaO, BaCO <sub>3</sub> , etc.....	4.7	19.2	30.4	33.5	32.0	31.0
BaSO <sub>4</sub> .....	29.7	38.7	40.4	34.0	34.0	33.8
Atomic ratio of $\frac{S}{Ba}$ by analysis.....	.96:1	.82:1	.72:1	.68:1	.70:1	.72:1
<b>Reduction:</b>						
Weight of charge (precipitate, kilograms.....	117.0	95.0	92.0	56.0	43.0	26.0
carbon, kilograms.....	20.0	16.0	15.0	10.0	7.2	4.0
Barium content, kilograms.....	66.2	61.7	55.1	29.8	23.6	14.8
Weight of product, kilograms.....	85.0	80.0	76.0	42.0	37.0	21.0
Barium, per cent of product.....	71.8	72.0	67.0	62.0	60.0	63.5
Barium content, kilograms.....	61.0	57.5	50.9	26.0	22.2	13.3
Barium lost in dust, per cent.....	7.9	6.8	7.6	12.7	6.0	9.5
Per cent of total barium in product, present as—						
Water-soluble BaS.....	75.0	48.6	48.2	40.5	44.3	49.5
Water-soluble BaO.....	6.9	11.1	6.1	3.4	4.5	4.0
Water-insoluble but acid-soluble compounds.....	14.6	31.3	41.5	51.1	46.7	44.2
BaSO <sub>4</sub> .....	3.5	9.0	4.2	5.0	4.5	2.3
Atomic ratio of $\frac{S}{Ba}$ in product by analysis.....	.80:1	.60:1	.58:1	.50:1	.52:1	.55:1

<sup>a</sup> Tests by A. E. Wells, A. L. Tuttle, W. Freeman, R. Buhman, C. E. Brandt, and V. P. Edwardes.

<sup>b</sup> Calculated for reaction between water-soluble BaS or BaO and SO<sub>2</sub>  
as per reactions  $2\text{BaS} + 3\text{SO}_2 = 2\text{BaS}_2\text{O}_3 + \text{S}$  and  $\text{BaO} + \text{SO}_2 = \text{BaSO}_3$

#### CYCLE OPERATIONS IN WHICH REDUCTIONS WERE MADE IN CRUCIBLES.

A cycle of operations was carried out in which the reductions were made in a crucible, the material thus being protected from contact with the products of combustion of the heating fuel. The temperature of the reductions was about 1,000° C. The amount of carbon used was 16 per cent of the weight of the barium compounds.

In the precipitations of the first five cycles the sulphur dioxide solutions used were strong, containing between 10 and 15 grams of SO<sub>2</sub> per liter. An excess of sulphur dioxide (about 0.5 gram per liter) was left in solution after each precipitation, and the reduced product added was allowed to remain in contact with the liquor for a considerable length of time—30 to 60 minutes. In the last three precipitations there was no excess sulphur dioxide left in solution after the first immediate precipitation of the barium sulphide and sulphur

dioxide. With these facts in mind, a study of the summary contained in Table 17 following, showing the reduction products, is interesting.

TABLE 17.—*Results of reduction tests with crucible involving eight cycles.<sup>a</sup>*

Cycle.	Material reduced.	Per cent of total Ba present as—			
		BaS readily soluble in H <sub>2</sub> O.	Insoluble in H <sub>2</sub> O, soluble in acid.	Insoluble BaSO <sub>4</sub> .	Reduced product No.
First....	Pure BaSO <sub>4</sub> by C.....	88.6	2.1	9.3	1
Second....	Precipitate formed by adding product 1 to SO <sub>2</sub> solution.	91.3	3.9	4.8	2
Third....	Precipitate formed by adding product 2 to SO <sub>2</sub> solution.	90.3	5.4	4.3	3
Fourth....	Precipitate formed by adding product 3 to SO <sub>2</sub> solution.	90.2	3.8	6.0	4
Fifth....	Precipitate formed by adding product 4 to SO <sub>2</sub> solution.	85.5	7.3	7.2	5
Sixth....	Precipitate formed by adding product 5 to SO <sub>2</sub> solution.	82.8	10.2	7.0	6
Seventh....	Precipitate formed by adding product 6 to SO <sub>2</sub> solution.	77.9	15.0	8.1	7
Eighth....	Precipitate formed by adding product 7 to SO <sub>2</sub> solution.	75.0	17.0	8.0	8

<sup>a</sup> Tests by W. Freeman and V. P. Edwards.

#### CONVERSION OF OXIDE AND CARBONATE IN REDUCED PRODUCTS TO SULPHITE OR SULPHATE.

From the results of tests made in cycles it was evident that in order to conduct the process most successfully it would be necessary to do one of two things—either to effect the reduction in an indirectly fired furnace, such as a muffle or a retort, whereby there would be formed the minimum amount of the water-insoluble barium compounds, or, if the reduction was effected in a direct fired furnace, to introduce some method of converting these barium compounds back to the sulphite or sulphate for their subsequent reduction to sulphide.

Some experiments were made to determine the conditions required for the conversion of the oxide and the carbonate to the sulphide by a reaction with sulphur dioxide in solution.

A typical experiment is summarized here to show the rate at which this conversion takes place.

A reduced product from the fifth cycle, from which the readily soluble barium sulphide and oxide had been leached out, was used. The residue contained 16 per cent of the barium as sulphide, 55 per cent as oxide, and 13 per cent as carbonate and silica, 4 per cent as sulphite, and 12 per cent as sulphate.

This material, pulverized to 100 mesh, was shaken vigorously for 20 minutes with a solution containing 9 grams of sulphur dioxide per liter. After filtration there was still excess sulphur dioxide in solution. The residue contained a trace of barium sulphide, and 40 per cent of the barium was still present as oxide. Considerable barium (not determined) had gone into the mother-liquor solution.

Another sample was pulverized to 200 mesh and shaken for one hour with a solution containing 6 grams of sulphur dioxide per liter. The sulphur dioxide present was in excess of that required for reaction with the barium sulphide and oxide in the sample to form normal sulphite. After the hour's shaking about 26 per cent of the barium had gone into the solution, and the residual barium still contained considerable, about 30 per cent, barium oxide.

From this and other similar experiments it was determined that there was little chance for converting these compounds to the sulphite in the regular precipitation process, unless the solutions were kept strong in sulphur dioxide or the time allowed for agitation was much longer than could be considered practicable.

Thus it was decided that in order to keep these compounds in the cycles it would be necessary to leach out the water-soluble compounds occasionally and treat the residue with fairly strong sulphur dioxide solutions in a separate apparatus.

Tests were made in which the water-insoluble residues were treated in an agitator or pebble mill with sulphur dioxide solutions of different strengths for varying periods of time. Stated briefly, the tests showed that these insoluble barium compounds when pulverized finely can be converted into sulphite and sulphate by agitation with a sulphur dioxide solution of about 1 per cent strength for several hours. When the action was facilitated by further grinding and agitation, as in a pebble mill, the action was fairly rapid. In this treatment some of the barium oxide was dissolved as a bisulphite, so that to save the barium in practice this solution would have to be returned to the precipitation system.

Dilute sulphuric acid also converted these barium compounds to the sulphate.

#### GENERAL SUMMARY AND CONCLUSIONS.

The results of the investigations herein described warrant the statement that every step of the wet Thiogen process can be controlled and carried out successfully on a small laboratory scale, and the indications are that the same success can be expected in the large-scale operations of a commercial unit. There are no factors to prevent the successful conduct of the following operations: Absorption of the sulphur dioxide gas by the mother liquor solutions, precipitation of the sulphur compounds by the addition of barium sulphide to the solutions, settling of the precipitate, decantation of the solution, dewatering or filtering of the precipitate, and distillation of sulphur from the dried precipitate.

In the reduction operation also there are no factors that prohibit the conduct of the process. It is true that in all reduction methods some sulphur is lost, resulting in the formation of oxides or carbonates of barium that react slowly in the precipitation operation. However,

the proportion of these insoluble barium compounds can be reduced to a low figure by rapid reduction with carbon at a high temperature in a furnace externally heated. If reductions are effected in a direct-fired furnace, the proportion of these compounds is greater. However, as these insoluble compounds increase in the cycles, the soluble barium compounds can be leached out and the insoluble compounds allowed to react with a strong sulphur dioxide solution, resulting in their conversion to sulphite and sulphate, which can be reduced to the sulphide.

Regarding the commercial feasibility of the process, the following points must be considered:

In the absorption operation it is necessary that the percentage of sulphur in the gases should be as high as possible. It seems probable that a gas concentration of less than 6 per cent should not be considered in practice. Furthermore, a fairly constant concentration of sulphur dioxide in the gases is necessary if concentrated solutions and a high absorption of the sulphur dioxide are to be attained at the same time.

The relative solubility of sulphur dioxide in solution at different temperatures must be considered also. At 33° C. (91° F.), the volume of solution required to absorb a given weight of sulphur dioxide would be about twice that at 11° C. (52° F.). Unless special cooling devices were introduced, the temperature of the mother liquor would be nearly that of the surrounding atmosphere, certainly not lower. Thus the cost of absorption would depend to a certain extent on the average temperature of the neighboring air.

The gas should also be cleaned of dust and fume before it is sent to the absorption tower, otherwise the solution will become foul with the soluble compounds and the precipitates will become contaminated with flue dust and other impurities.

The operations of precipitation, settling, decantation, filtering, drying, and distillation called for in this process should not be any more difficult to conduct on a commercial scale than similar operations now carried on in standard commercial apparatus.

However, the efficiency of the settling, decantation, and filtering operations are largely dependent on the conditions under which the precipitation takes place. Thus, it is necessary that the sulphur dioxide content of the solutions coming from the absorption tower should be fairly constant, or the constant attention of an attendant will be necessary to see that the solutions are not too acid or alkaline after precipitation. This part of the process will probably require careful supervision.

In the commercial operation of the reduction process the tendency for the formation of insoluble barium products must be considered an important factor.

To reduce the amount of these insoluble compounds to a minimum the reduction must be effected rapidly, with carbon at a high temperature, and out of contact with the furnace gases. This would necessitate reduction in a muffle type furnace. At the high temperature required, such reduction would be more expensive to carry on than a reduction in a direct-fired furnace, as for example in a multiple-hearth furnace or in a cement kiln.

Even with this type of reduction, in a commercial application of the process, there would be a gradual accumulation of these "inactive" barium compounds, which would require special treatment with strong sulphur dioxide solutions or dilute sulphuric acid for conversion to compounds that could be reduced to the sulphide.

If the reduction is to be effected in a direct-fired furnace the necessity will be still greater for a supplementary operation to convert the barium oxide or carbonate to the sulphite or sulphate. However, by the introduction of this conversion operation the loss of barium as insoluble compounds through a series of cycles can be reduced to a low figure.

Another possible method of handling some of these water-insoluble but acid-soluble barium compounds would be to dissolve them in dilute acid after the water-soluble sulphide and oxide had been leached out, and thus prepare barium salts for the market.

Reducing the precipitate in a direct-fired furnace would involve in each cycle a loss of at least 5 per cent of the barium as dust, unless the dust was precipitated by the electrical precipitation or a similar process.

The results of the laboratory study of the wet Thiogen process demonstrate that the technical operation of the process can be carried out successfully for the recovery of sulphur from sulphur dioxide in waste smelter gases, and the indications are that at least in some localities the process can be applied on a commercial scale and sulphur recovered at a cost that will allow a profit.

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The writer also wishes to express his appreciation of the ready cooperation and valued counsel of Dr. L. H. Duschak, chemical engineer, Bureau of Mines.

## **APPARATUS REQUIRED AND MATERIAL HANDLED TO PRODUCE 10 TONS OF SULPHUR A DAY.**

Based on the results of the critical study of the Thiogen process herein described, an outline has been prepared showing the apparatus required and the approximate quantities of material to be handled in the production of 10 tons of sulphur a day by the wet Thiogen process.

In this outline it is assumed that—

The furnace gases contain 7 per cent SO<sub>2</sub>.

The furnace gases are delivered at the absorption tower at 20° C. and free from dust and fumes.

The temperature of the mother liquor can be maintained at 20° C. or less.

An absorption of 80 per cent of the total sulphur dioxide in the gases is satisfactory.

Reduction is effected in a cement kiln.

Dust from the cement kiln is recovered by the electrical precipitation apparatus.

In the precipitation process no attempt is made to effect a reaction between the comparatively insoluble barium compounds and the sulphur dioxide by allowing excess sulphur dioxide to be present in solution after the readily soluble compounds have reacted. These insoluble compounds are to be converted to the sulphite or sulphate by a supplementary process.

### **DETAILS REGARDING PARTS OF APPARATUS.**

Prescribed details regarding parts of the apparatus are given below in semitabular form.

#### **ABSORPTION TOWER.**

Total volume of gases to tower per minute at 20° C., 2,650 cubic feet.

Total SO<sub>2</sub> in 2,650 cubic feet, 31 pounds per minute.

SO<sub>2</sub> absorbed in tower, 25 pounds per minute.

If the tower is constructed on the same lines as was the experimental tower, it would have the following dimensions: Total area of cross section, 70 square feet; area of space through the grill work, 25 square feet; total height, 50 feet.

The absorption height may be provided by single tower, or, as planned by the Thiogen Co., by three towers, with the circulation of part of the solution through the middle tower to build up the concentration. The length of time of contact of the gases and the solution would be about the same in either case.

The volume of mother liquor at 20° C. required to absorb this weight of sulphur dioxide would be about 38 cubic feet, or 277 gallons. The resulting solution would contain 25 pounds of SO<sub>2</sub>.

#### REGULATING TANK.

Mother liquor to flow by gravity from absorption tower to regulating tank.

Tank to be covered to prevent loss of SO<sub>2</sub>.

Dimensions: Diameter, 8 feet; height, 4 feet; capacity, 100 cubic feet, or 748 gallons.

#### PUMP.

Pump to force 277 gallons of solution per minute from regulating tank to agitator.

#### INCORPORATOR AND MIXER.

An automatic incorporator, as, for example, an adjustable worm-screw feed, would be required by which the proper proportion of the reduced material could be added to all, or a part, of the mother liquor as it is pumped from the regulating tank to the agitating tank. If the sulphur dioxide concentration of the solution can be maintained nearly constant, such an automatic incorporator would not require much close attention on the part of attendants. Centrifugal pumps are effective mixers.

Assuming that the average reduced product to be incorporated contains not less than 70 per cent BaS, 63 pounds of reduced material containing 44 pounds of BaS plus 19 pounds of other compounds not reacting with SO<sub>2</sub> are to be incorporated per minute.

#### AGITATING TANK.

The agitating tank, such as a Dorr agitator, should have a capacity of about 1,200 cubic feet (9,000 gallons), or the equivalent of about 30 minutes' supply of solution. Agitation should be vigorous and accomplished by mechanical means, as by paddles, rather than by compressed air. The overflow from the agitator should flow to settling tanks.

#### SETTLING TANKS.

Two tanks in series, each with a capacity of about 1,000 cubic feet (7,450 gallons), or a total settling capacity equivalent to 50 minutes' supply of solution.

Tanks should be equipped with slowly revolving rabbles, arms and rabbles to move precipitate to a center discharge at bottom.

A settled precipitate containing 50 per cent water may be obtained. In fact, the precipitate may be so thick as to require a special pump for moving it to a filter.

Total weight of precipitate to be settled per minute, 88 pounds, or 63.5 tons a day.

Mother liquor flowing to pump to be returned to absorption tower by pump; will contain some light, flaky sulphur, which will not clog in the pump nor settle in the tower.

#### FILTERS.

Filters must handle daily 126 tons of settled precipitated sludge containing not over 50 per cent water. With a vacuum of 18 inches a 1½-inch cake can be obtained in three minutes. Filtered cake should contain less than 25 per cent water. Discharge from filter should go into conveyor to be run onto drying furnace.

#### PUMPS.

Pumps to handle 250 to 270 gallons of mother liquor per minute from the overflow of settling and from the filter to the top of the absorption tower—approximately a 60-foot head.

#### DRYING FURNACE.

Material to be dried daily, 84.5 tons containing a maximum of 25 per cent water. Because of the necessity of drying at comparatively low temperatures, a steam drier

would probably be necessary. It is estimated that the gases from the reduction furnace, if burned under a boiler, should furnish sufficient heat energy to carry on the drying operation.

#### DISTILLING FURNACE AND CONDENSER.

Sixty-three tons of dried precipitate per day must be heated to 450° C. in a distilling furnace, and 10 tons of sulphur distilled. For this purpose a muffle-type furnace, equipped with rabbles or other stirring devices, may be used. A revolving cylindrical retort also might be employed. The circulation of a stream of sulphur dioxide through the distilling furnace into the condenser will facilitate the distillation of sulphur.

The daily fuel consumption, unless waste heat were available, would probably be 3 to 4 tons of coal, or 12 to 16 barrels of oil, depending on the construction of the furnace. However, the waste heat from the reduction furnace can also be utilized for the distillation and the actual fuel consumption would be much less. Coke or coal could not be mixed with the material to be heated in the distilling furnace, for there would result the formation of some carbon-sulphur compounds, or compounds of sulphur and hydrocarbons, which would reduce the purity of the sulphur condensed.

The residue consists of barium sulphate, sulphate, oxide, carbonate, and possibly some sulphide. It is pulverulent and is ready for mixing with the pulverized coal or coke.

#### PULVERIZER FOR COAL OR COKE AND MIXER.

Coke or coal, pulverized to at least 160 mesh, or lampblack carbon must be mixed intimately with the residue. Fifteen per cent fixed carbon should be provided. Mixing may be accomplished in a tube mill, as the material is taken from the distilling furnace and is then sent directly to the reduction furnace, thus saving heat.

Residue from distilling furnace, 53 tons. BaSO<sub>3</sub> and BaSO<sub>4</sub> present, 45 to 48 tons. Carbon to be mixed, 6 tons of coke, or 13 tons of coal.

#### REDUCTION FURNACE.

The daily charge to the reduction furnace would be 53 tons of barium compounds, containing 45 to 48 tons of BaSO<sub>3</sub> plus BaSO<sub>4</sub>, with 6 tons of carbon, as coke, or 13 tons as coal.

The maximum temperature desired in the furnace would be about 1050° C. In order that the reduction be accomplished most effectively, the material should be heated rapidly to 850° C. or higher and should be put through the furnace in a short time.

Rather than realize in the reducing furnace the maximum heat value of the fuel burned in the furnace it would probably be preferable and most economical to allow the furnace gases to leave the reducing furnace while still very hot, that is, about 500° C. This waste heat could then be utilized in the distilling furnace or in a boiler, and at the same time any combustible gases present in these gases could be burned to furnish steam for the drying operations.

A cement kiln about 70 feet long and 7½ feet in diameter would probably handle the material in 24 hours. For this purpose the fuel consumption would be about 6 tons of bituminous coal with a heating value of about 12,000 British thermal units per pound, or 20 barrels of crude oil per day.

If reduction was affected in a muffle type furnace, the fuel consumption would undoubtedly be almost twice as great as in a direct-fired furnace. If estimates of the fuel consumption are based on the current practices of muffle-furnace reductions, a fuel consumption of one-third of a ton of coal per ton of material reduced would be very low. This would mean 15 to 16 tons of coal per day for carrying on the reduction in the muffle furnace.

**ELECTRICAL PRECIPITATION APPARATUS.**

Electrical precipitation apparatus, to handle approximately 10,000 cubic feet of gas per minute at 450° C., and to recover about 2 tons of dust per day.

**PULVERIZER.**

The reduced material, 35 to 40 tons, must be pulverized to at least 80 mesh before it can be used as a precipitant satisfactorily. The finer the material is ground, the more readily will the comparatively insoluble products react with sulphur dioxide in the solution.

**LEACHING TANK.**

It would be necessary to provide for leaching the water-soluble compounds from the reduced material whenever the proportion of the barium sulphide was reduced to 60 or 65 per cent of the total. If the reductions are effected in a cement kiln it would probably be necessary to leach 4 or 5 tons of material a day. The solution of barium sulphide would have to be returned to the agitation tank or to the precipitation tank.

**AGITATING TANK.**

Agitating tank for converting barium oxide to sulphite or sulphate, to handle 3 or 4 tons a day.

This tank would have to be covered to prevent the escape of sulphur dioxide gas. A ball or pebble mill would be effective for this operation.

**CONSTRUCTION COST.**

An estimate of the cost of construction of a 10-ton plant equipped as above outlined, with all the necessary accessories, based on the cost of material, etc., in 1913, indicates that the cost would be about \$40,000.

**ESTIMATED COST OF PRODUCTION.**

An estimate of the cost of production of sulphur from such an installation producing 10 tons a day has been made, based on costs of material and labor as follows:

*Costs of material and labor used as basis for estimate of cost of production of sulphur from 10-ton plant.*

## Fuel:

Coal, per ton.....	\$3.00
Oil, per barrel.....	.80

## Reducing agent:

Coal, per ton.....	3.00
Lamblack, carbon, or coke, per ton.....	6.00

Barium sulphate, per ton.....	7.50
Power, per horsepower hour.....	.007

## Labor:

Common, per day.....	2.50
Skilled, per day.....	3.50

The detailed estimate of the cost of production of sulphur follows:

*Detailed estimates of cost of production of sulphur from 10-ton plant.*

Power, including power for pumping solutions and precipitate sludge, for operating incorporator, agitator, filter, drying furnace, pulverizer, mixer, and reduction kiln, and for causing gases to circulate through absorption towers.....	\$6.00
Fuel and reducing carbon.....	60.00
Labor:	
1 skilled operator per shift at \$3.50.....	\$10.50
2 attendants per 8-hour shift at \$2.50.....	15.00
1 furnace man per shift at \$3.....	9.00
	— 34.50
Barium sulphate, unavoidable loss.....	5.00
Interest (6 per cent) and depreciation (including repairs), 16.5 per cent.....	24.50
Total.....	130.00
Cost per ton of sulphur.....	13.00

With a larger plant, some of these items, especially that of labor, would be somewhat decreased per ton of sulphur produced. With a 20-ton plant, the cost would be about \$12 per ton.

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